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13. ABSTRACT (Maximum 200 words)  <b>The overall objective is to connect the near surface behavior of a model pressure sensitive adhesive with its macroscopic adhesive performance. Work with a new tackifier suggested that for complex commercial tackifiers the mixture of species in the tackifier may benefit miscibility. When miscibility is impaired, aging phenomena become more prominent. Force-distance measurements made at different frequencies can reveal viscoelasticity effects in such adhesives, but the frequency range that can be studied is limited.</b> <b>X-modulation is an excellent technique for probing differences in mechanical properties of adhesive surfaces. For example, changes due to enrichment of the surface by a lower molecular weight species can be detected. However, a characterization protocol combining X-modulation with a force-distance measurement is superior, yielding better reproducibility, higher precision, and more information in one experiment. Using contact mechanics and simplifying assumptions, estimates of modulus at the surface have been made. The new protocol was also demonstrated by characterizing changes in surface behavior with humidity. Humidity effects were most pronounced with the aged model adhesive that we had already shown to have the most strongly adhesive surface of the blends of various tackifier composition. The observed changes with humidity are consistent with the contention that the surface is enriched in tackifier.</b>				
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## 1.) LIST OF MANUSCRIPTS AND PAPERS PRESENTED

### a.) Manuscripts submitted, but not published:

S. Moon, M.D. Foster, "Influence Of Humidity On Surface Behavior Of Pressure Sensitive Adhesives Studied Using Scanning Probe Microscopy," submitted to *Langmuir*.

### b.) Papers published in peer-reviewed journals

1. S. Moon, M.D. Foster, " Near Surface Nanomechanical Behavior of Pressure Sensitive Adhesives Using Lateral Modulation Scanning Probe Microscopy," *Langmuir* **18**, 1865-1871, 2002.
2. S. Jia, M.D. Foster, "Resolving Lateral Variations in the Frequency Dependence of Adhesive Properties at the Surface of a Model Pressure Sensitive Adhesive," *J. Applied Polym. Sci.* . **84**, 400-404, 2002.
3. A. Paiva, N. Sheller, M.D. Foster, A. J. Crosby, K.R. Shull, "Microindentation and Nanoindentation Studies of Aging in Pressure Sensitive Adhesives," *Macromolecules*, **34**(7), 2269-2276, 2001.

### c.) Papers published in non-peer-reviewed journals or in conference proceedings

- 1.) S. Moon, M.D. Foster, "Scanning Probe Microscopy Study of PSAs: Recent Developments", Pressure Sensitive Tape Council Meeting, Atlanta, Georgia, May 1-3, 2002
- 2.) S. Moon, M.D. Foster, "Scanning Probe Microscopy Studies of Pressure Sensitive Adhesives," Adhesion Society Mtg Proceedings, Orlando, Florida, Feb. 2002
- 3.) S. Moon, S. Jia, M.D. Foster, "Scanning Probe Microscopy Studies of Pressure Sensitive Adhesives, Adhesion Society Mtg Proceedings, Williamsburg, February, 2001
- 4.) Adriana Paiva, M.D. Foster, Shijun Jia, Alison Szczecinski, A.J. Crosby, K.R. Shull, "Studying Changes in Surface Adhesion of PSAs with AFM and Spherical Indenter Tests," Adhesion Society Meeting, Myrtle Beach, SC, February 20, 2000.

### d.) Papers presented at meetings, but not published in conference proceedings

- 1.) Seung-ho Moon, Mark D. Foster, "Near Surface Nanomechanical Behavior of Pressure Sensitive Adhesives Using Lateral Modulation Scanning Probe Microscopy" The University of Akron, Department of Polymer Science Sponsors Day, October 13, 2001.
- 2.) Seung-ho Moon, Mark D. Foster, "Dynamic Viscoelastic Properties of Pressure Sensitive Adhesives by Force Modulation AFM," University of Akron, Department of Polymer Science Sponsors Day, October 13, 2000.
- 3.) Shi-Jun Jia, Mark D. Foster, Alison M. Szczecinski, "The Near Surface Behavior of Model Pressure Sensitive Adhesives Studied by Scanning Probe Microscopy," University of Akron, Department of Polymer Science Sponsors Day, October 13, 2000.

### e.) Presentations at organizations, institutions

- 1.) Mark D. Foster, "Near Surface Nanomechanical Behavior of PSAs Measured Using Lateral Force Modulation Atomic Force Microscopy," tesa AG, Hamburg, Germany, June 20, 2001.
- 2.) Mark D. Foster, "POLYMER THIN FILMS: Interface Dominated Behavior," Mt Union College, Alliance, OH, September 11, 2001.
- 3.) Mark D. Foster, "Frontiers in Polymer Surfaces and Interfaces," Frontiers in Polymer Science and Polymer Engineering Short Course, The University of Akron, Akron, OH May, 2001.
- 4.) Mark D. Foster, "Studying Model Adhesive Blends by Scanning Probe Microscopy," Beiersdorf AG, Hamburg, Germany, September 1, 2000.
- 5.) Mark D. Foster, "Studying Pressure Sensitive Adhesives by Scanning Probe Microscopy," Avery Dennison, Painesville, OH, May 12, 2000.
- 6.) Mark D. Foster, "Frontiers in Polymer Surfaces and Interfaces," Frontiers in Polymer Science and Polymer Engineering Short Course, The University of Akron, Akron, OH May 10, 2000.

- 7.) Seung-ho Moon, Mark D. Foster, "Scanning Probe Microscopy Studies Of Pressure Sensitive Adhesives," 24<sup>th</sup> Annual Technical Seminar of the Pressure Sensitive Tape Council , May 2-4, 2001, Orlando, FL. **Won Award for Best Poster Presentation\***
- 8.) Mark D. Foster, "Scanning Probe Microscopy Studies of Model Pressure Sensitive Adhesives," Microscopy Society of Northeast Ohio, Brecksville, OH, March 7, 2000.
- 9.) Adriana Paiva, Mark Foster, Alfred Crosby, Ken Shull, "Studying the Surface Adhesion of Pressure Sensitive Adhesives with Atomic Force Microscopy and Spherical Indenter Tests, " AIChE National Meeting, Dallas, TX, 31 -Nov. 1, 1999. **Won Award for 2nd Place in Student Poster Competition.**

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#### **PARTICIPATING SCIENTIFIC PERSONNEL**

Dr. Mark D. Foster, Professor

Dr. Shijun Jia, Postdoctoral researcher (moved to U. Pittsburgh in mid '01)

Seung-ho Moon, Ph.D. Candidate

Brandon Barrett, Summer undergraduate researcher, (Supported by a gift to the department's summer intern program)

Rick Batman, Ph.D. candidate (part-time, supported by the Physics department)

Allison Szczecinski, M.S. candidate, graduated Dec. 1999

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#### **INVENTIONS**

None

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#### **PRIZES, HONORS**

Seungho Moon - Best Poster Presentation at 24<sup>th</sup> Annual Technical Seminar of the Pressure Sensitive Tape Council , May 2-4, 2001, Orlando, FL.

Adriana Paiva - 2<sup>nd</sup> place, Student Poster Competition,. American Institute of Chemical Engineers. National Meeting, Dallas, TX, Oct. 31-Nov. 5, 1999

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## SCIENTIFIC PROGRESS AND ACCOMPLISHMENTS

### Executive Summary

- 1.) Investigated the behavior of a model pressure sensitive adhesive with higher molecular weight tackifier.
- 2.) Demonstrated that the viscoelastic character of the tackified adhesive manifests itself in force-distance measurements of the adhesive made at varying frequencies. Quantification and extension over a broad range of frequency is hindered by piezo hysteresis effects.
- 3.) Made first measurements of nanomechanical surface properties with x-modulation for the purpose of identifying surface segregation in a polymer blend driven by molecular weight alone.
- 4.) Improved speed, precision, and reproducibility of measurement of surface mechanical properties by x-modulation experiments by implementation of fully automated data acquisition.
- 5.) Further improved quality of surface mechanical characterization by combination of x-modulation with force-distance curve measurement.
- 6.) Accomplishments 3,4,5 above are broadly applicable to polymer-containing systems including polymer blends, nanocomposites, and other hybrids.
- 7.) Showed that the nanomechanical response of the surface of an aged, tackified, model PSA is much more sensitive to humidity than is the response from the corresponding pure polymer. It appears that both capillary bridging between the tip and the surface and plasticization of the tackifier-enriched surface could be playing roles in this behavior.
- 8.) The model adhesive with the strongest adhesion at surface also has the surface properties most sensitive to humidity.

### Introduction

Scientific accomplishments from the entire grant period will be reviewed. The results are most readily discussed by considering, in turn, seven different portions or major developments of the work. The topics of the following sections are:

- 1.) the effect of tackifier molecular weight on PSA behavior,
- 2.) probing surface mechanical properties on the nanoscale using X-modulation,
- 3.) studying the frequency dependence of the adhesive behavior with SPM,
- 4.) detection of surface segregation due to molecular weight alone using X-modulation,
- 5.) studying humidity effects with X-modulation,
- 6.) characterization of surfaces using X-modulation combined with a force-distance curve, and
- 7.) studying humidity effects with X-modulation combined with force-distance measurement.

Conclusions are stated briefly at the end of each section.

### 1.) Effect of Tackifier Molecular Weight

In order to consider further the effect of tackifier structure on the near surface behavior of model adhesives a tackifier was considered that is analogous in chemical structure to the n-butyl ester of abietic acid already studied, but larger<sup>1</sup>. This diester, for which the structure is shown in Figure 1, has both higher molecular weight ( 667 g/mole) and higher glass transition temperature (10°C) than does the monoester. Thus this model tackifier is more nearly typical, in some ways, of the most widely used, commercial rosin based tackifiers than is the monoester. The diester proved to be strongly immiscible with amorphous poly(ethylenepropylene) (PEP) ( 390,000 g/mole,  $M_w/M_n = 1.1$ ). Samples made with polyisoprene (PI) of narrow molecular weight distribution (320,000 g/mole,  $M_w/M_n = 1.1$ ) appeared to be miscible when first cast, but showed evidence of immiscibility at the surface of the adhesive after periods as short as five days. This was surprising, since the monoester is miscible with this PI and a commercial tackifier, Pentalyn H, that contain pentaerythritolester of hydrogenated abietic acid is also miscible with PI. ***It appears that the complex mixture of species having different molecular weights and chemical structures is key in the miscibility of the Pentalyn H with PI.***

Samples for investigation by scanning probe microscopy (SPM) were prepared by solution casting on microscope slides using an Accu Gate™ fluid spreader. Film thickness ranged between two and three mils (50 to 75  $\mu\text{m}$ ). SPM measurements were performed using the Autoprobe™ M5 or CP by Park Scientific Instruments. SPM experiments allowed the determination of a film's adhesive properties as well as the study of

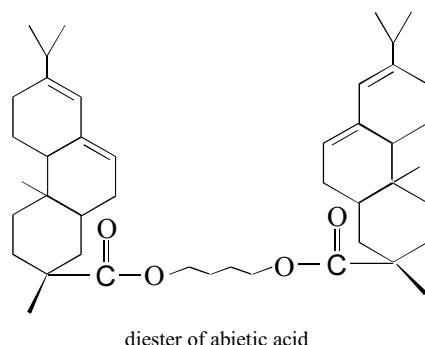


Figure 1. Chemical structure of the diester of abietic acid.

the topography of the sample. Topographic and friction images of sample's surface were obtained under ambient conditions according to established procedures. Local adhesive and viscoelastic properties were measured by indenting the surface with the tip and recording cantilever deflection as a function of tip to sample distance (force-distance measurements). Silicon probes (Ultralever™, Park Scientific Instruments) with V-shaped cantilevers and conical tips with typical radii of curvature of approximately 10 nm were used for all measurements (as reported by the manufacturer).

Study of the surface morphology of PI/DEAA samples using SPM focused on two compositions, 15 and 45 wt % DEAA. For tackifier loadings higher than 45 wt % the surfaces were so rough that they were difficult to image. The PI/DEAA adhesives were not as tacky as the PI/nBEAA blends in the as-cast state and already at two weeks SPM images could be obtained in both contact and light tapping mode. Light tapping mode images

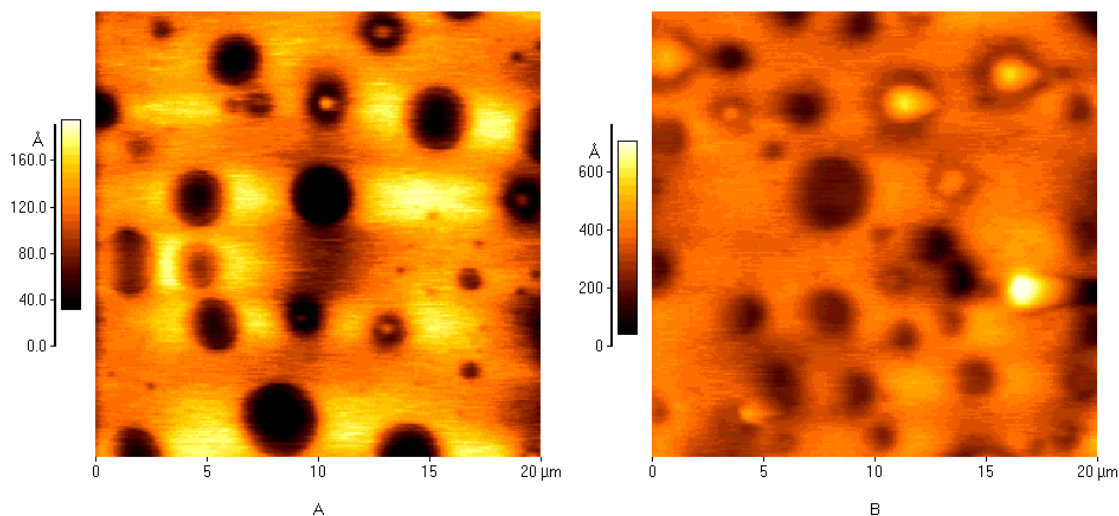


Figure 2. SPM light-tapping mode topographic images of the surfaces of model adhesives containing PI and DEAA with tackifier loadings of a.) 15 and b.) 45 wt % . The samples are two weeks old.

of the surfaces of two week old samples (aged in ambient temperature and humidity) are shown in Figure 2. A two phase morphology is evident at the surface at both compositions. For the 45 wt % sample the surface was also imaged in contact mode as shown in Figure 4. When the topography was measured in contact mode, a lateral force image could be obtained simultaneously. It is important to note that for this system the lateral force measured on the domains was lower than that of the surrounding matrix. X-modulation results obtained later on the PEP/nBEAA system suggest that this is due to differences in deformability between the matrix and domains.

Study of the aging in PI/DEAA blends revealed several differences from the behavior seen in PEP/nBEAA blends or PI/nBEAA blends. The topography of PI/DEAA blends with 45 wt% tackifier changed markedly over a period of a few weeks and became very rough. Initial differences in the lateral force measured on the domains and matrix region disappeared with time. Very strong differences in the force-distance curves of the matrix and domains also were eliminated by aging.

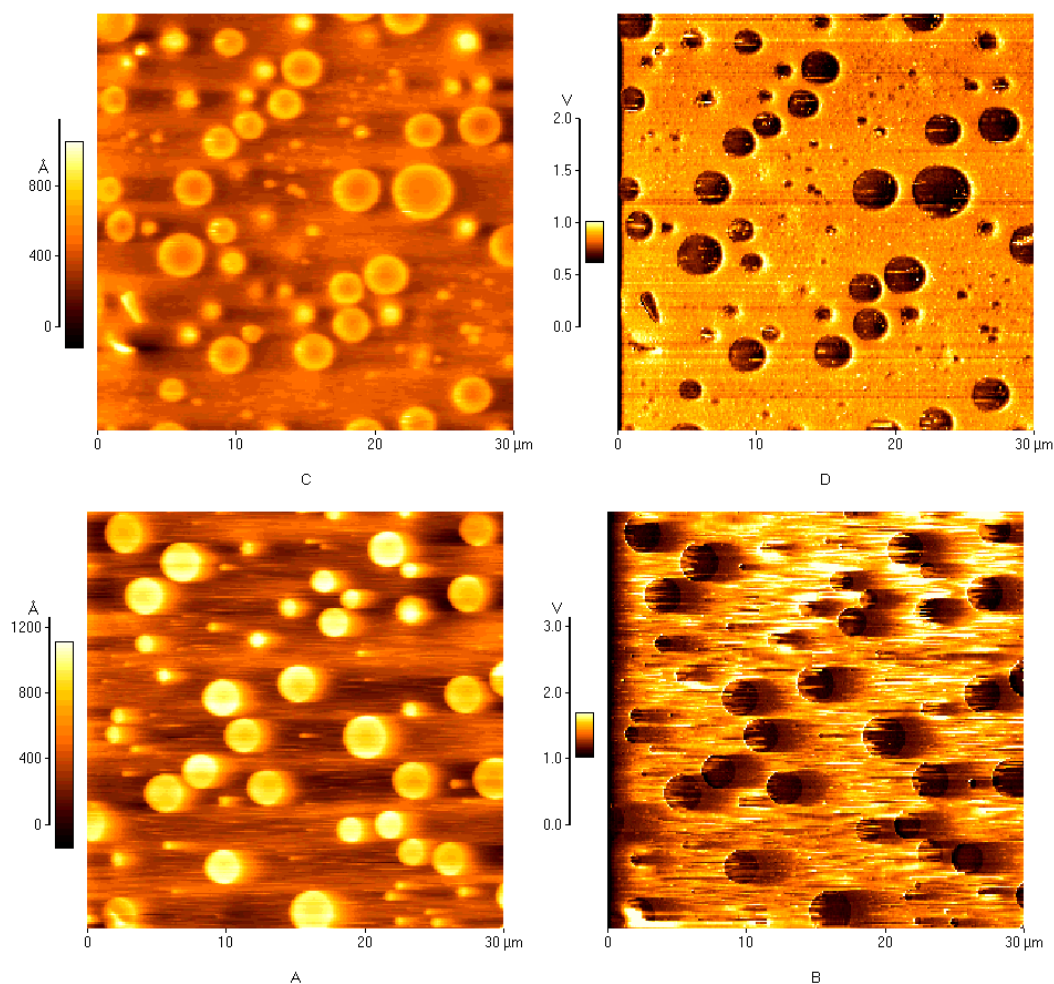


Figure 3. Changes in surface morphology measured in contact mode and lateral force images of PI/DEAA adhesives with time for a tackifier loading of 15 wt %. Topographic images are on the left and lateral force images on the right. The top row images were taken at four weeks and the second row images at six weeks. The images taken at different times are *not* from the same spot on the sample.

Imaging was done at two, four, five and six weeks. Examples of the changes observed are sampled in Figures 3 and 4. The morphology of the sample with 15 wt % changed only modestly with time. Discreet domains were seen. In contrast the morphology of the sample with 45 wt % tackifier changed markedly. At two weeks age discreet domains could be readily seen at the surface and the lateral force measured on the



domains was markedly lower than that of the surrounding matrix. After four weeks it became difficult to identify a "matrix" in topographic images of the surface and differences in friction of the various regions at the surface were small. The topographic and lateral force images at four and six weeks were similar in character.

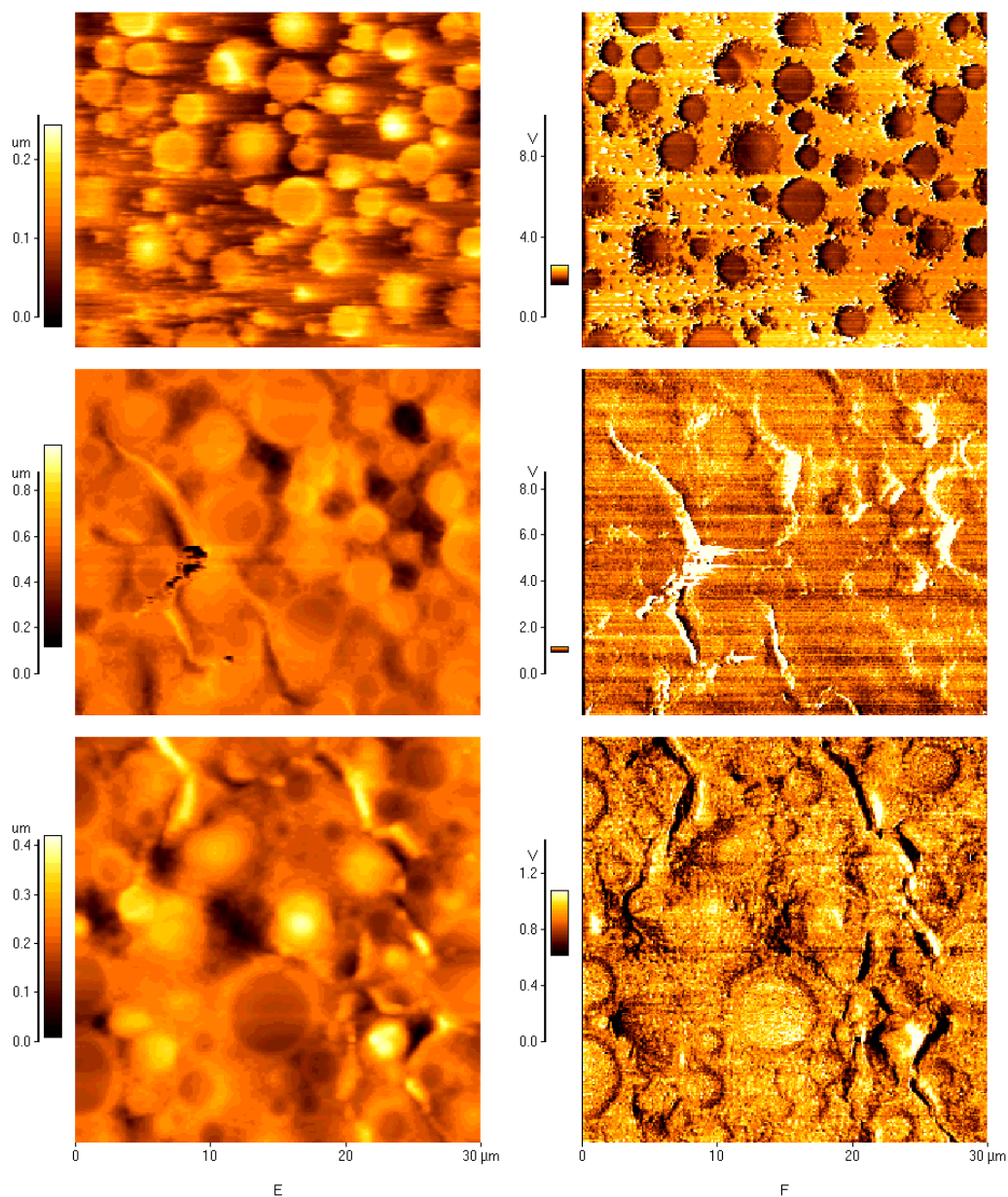


Figure 4. Changes in surface morphology measured in contact mode and lateral force images of PI/DEAA adhesives with time for a tackifier loading of 45 wt %. Topographic images are on the left and lateral force images on the right. Each row of images corresponds to a different age of the sample, top (A, B): two weeks, middle (C,D): four weeks, bottom (E,F): six weeks. The images taken at different times are *not* from the same spot on the sample.

**Table 1: Change in surface roughness with aging**

Age (weeks)	Mode	15 wt %	45 wt %
2	Light tapping	34 Å	73 Å
2	contact	NA	420 Å
4	contact	230 Å	837 Å
6	contact	135 Å	533 Å

The surface roughnesses (Table 1) calculated from the topographic images were large for both the 15 wt% and 45 wt% samples, but larger for 45 wt %. In fact, the very large roughnesses of samples containing the higher loading of DEAA made it very difficult to image those samples.

The force-distance curves taken from the samples changed markedly with aging. As with the PEP/nBEAA samples, different F-d curves are seen for the domain and matrix regions of the sample surface. Curves from the two types of regions are shown in Figure 5 for the case of the sample with 15 wt % DEAA at six weeks. The matrix is soft and sticky. The domain is much stiffer, but shows nonetheless an appreciable pull-off force. These curves were measured using the same protocol as used in previous work. The shape of the loading curve for the matrix is affected by the fact that adhesive from the surface is still stuck to the tip from the imaging that is done right before making the force distance measurement. A protocol developed subsequently eliminated this artifact.

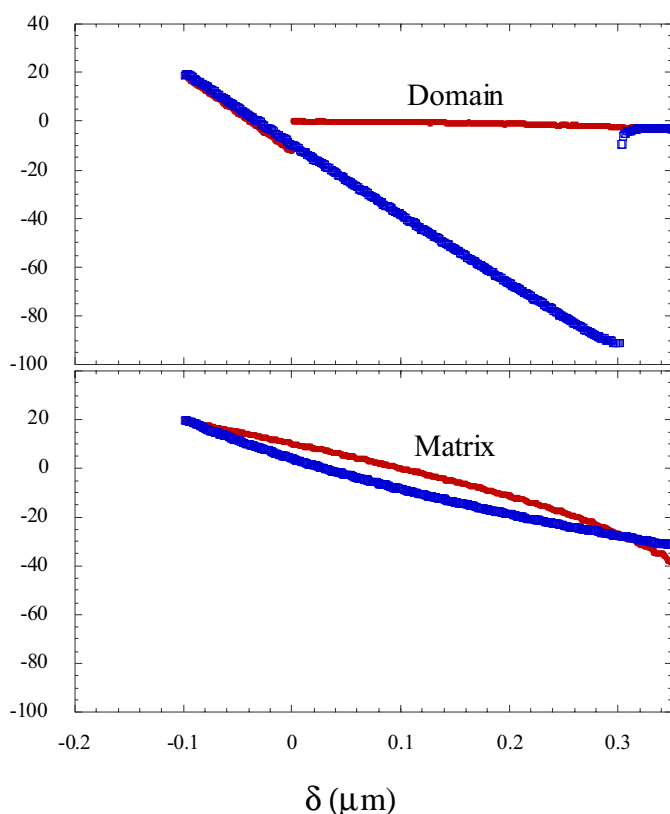


Figure 5. F-d curves from the matrix and a domain of the PI/DEAA sample with 15 wt % tackifier at six weeks.



Figures 6 and 7 demonstrate how the F-d curves for the sample with 45 wt % DEAA change with age over a ten week period. The change in the matrix is quite dramatic. At two weeks the sample is very soft and sticky. The material becomes stiffer with time and less adhesive as seen by the reduction in the area between the loading and unloading curves and the reduction in pull-off force.

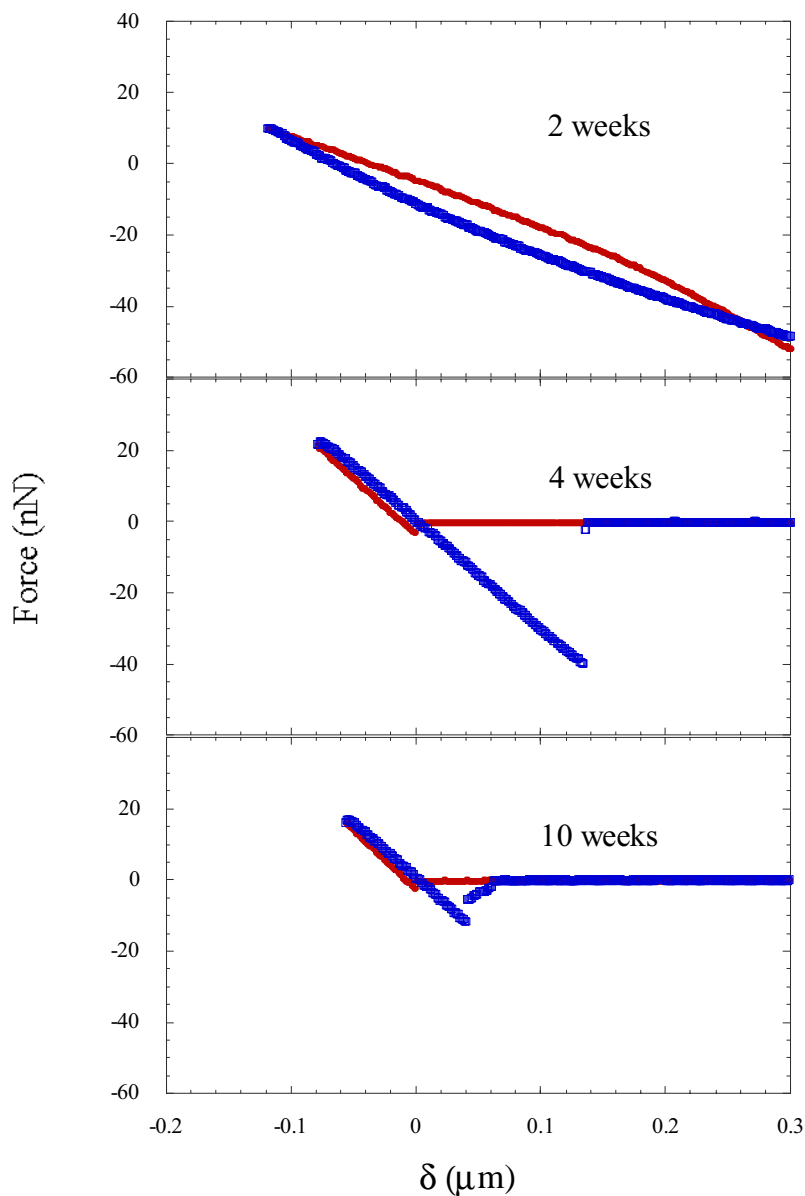


Figure 6. Change with aging for the F-d curves measured in the matrix regions of the sample containing 45 wt % DEAA. Sample age is marked inside each plot.

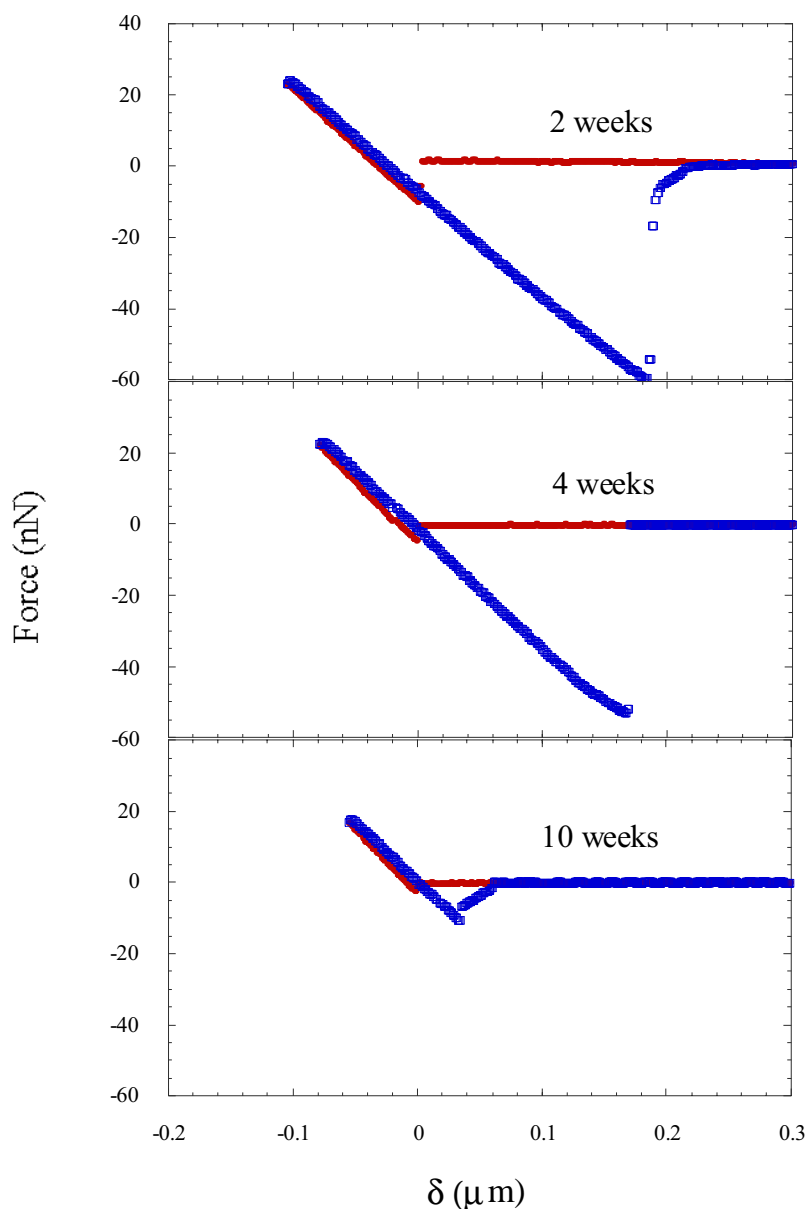


Figure 7. F-d curves measured in the domains change with aging of the sample. Shown here are curves for the PI/DEAA sample with 45 wt % DEAA measured at two, four, and ten weeks. At ten weeks the distinction between "matrix" and "domain" is no longer meaningful. The same behavior is seen everywhere on the surface.

**Conclusions:** When a tackifier of structure and molecular weight more similar to that of the "average" commercial tackifier molecule is used in a model PSA with polyisoprene, miscibility is adversely affected. Apparently the complex mixture of species having different molecular weights and chemical structures in the commercial tackifier Pentalyn H is key to its miscibility with PI. The immiscible blends with the diester ags more prominently than do corresponding PI/nBEAA adhesive blends, with the surface becoming very rough after a few weeks. After ten weeks the force-distance behavior of the "domain" and "matrix" regions of the surface are indistinguishable.

## 2.) Studying Frequency Dependence of the Adhesive Behavior with SPM

We studied systematically the frequency dependence of the force-distance curve behavior for adhesives for the first time using the PI/DEAA system. PSAs blends were made with 15, 30, 45, 60 and 80 wt% DEAA.<sup>1</sup> For the demonstration of the frequency dependent effects that can be studied with SPM we focus here on the blend with 15 wt % additive. Its structure is shown in Scheme 1. Szczecinski<sup>1</sup> performed differential scanning calorimetry scans on samples five days after casting using a TA 2910 DSC and scanning from -100 to 40°C at 10 °C/min. Glass transition temperatures were determined from the first run and verified by the second run. For the sample with 15 wt % only a single transition could be clearly discerned at a temperature (-61°C) only slightly higher than the  $T_g$  of the pure PI. However, the transition was considerably broader in the blend and it has been assumed here that this transition temperature is characteristic of the polymer-rich matrix. Films cast from toluene solution for this study had thicknesses of about 50  $\mu\text{m}$ .

SPM imaging and force-distance measurements were performed when the samples were two weeks old using commercial Ultralever<sup>TM</sup> silicon probes with V-shaped cantilevers under ambient conditions. The corresponding force constant was experimentally determined to be about 0.4 N/m following the procedure of Tortonese *et al.*<sup>2</sup> The dynamic mechanical properties of the PSAs were probed qualitatively by observing changes in the shape of the F-D curve when changing frequency from 0.01 to 1 Hz. To obtain each F-D curve the piezo underneath the sample was first extended 0.04  $\mu\text{m}$  to collect the "loading curve" and then retracted a distance of 2  $\mu\text{m}$  to collect the "unloading curve". The large retraction distance was necessary due to the tendency for the sample to adhere tenaciously to the probe tip over a long distance upon retraction.

Figures 8 and 9 show the F-D curves obtained at sweep frequencies of 1, 0.5, 0.1 and 0.01 Hz from the PI enriched matrix and tackifier enriched domains, respectively, of a sample with 15wt% diester. The overall shape of the F-D curve varies with frequency. Loading curves for the tackifier-rich domains are all essentially vertical, indicating that the contact stiffness of the domains exceeds that of the cantilever at all frequencies considered. The maximum penetration depths change markedly for reasons explained below. For three frequencies the unloading curves are essentially straight, with a slope dictated by the stiffness of the cantilever. Only at the lowest frequency is changing of the slope characteristic of relaxation of the domain seen. In each case pull-off is abrupt, with the maximum pull-off force observed at the highest frequency.

For PI-rich matrix, the unloading curve exhibits continuous deformation over a large retraction distance in each case. As frequency is increased the surface behaves as though it were more stiff<sup>3</sup>. The slopes of the linear portions of the loading curves and the slopes of the initial portions of the unloading curves both increase. The slope of the initial portion of the loading curve is the best indicator of stiffness upon retraction because there the contact area is thought to change least rapidly. Steeper slopes correspond to higher apparent moduli, though to obtain quantitative comparisons<sup>4,5</sup> one must account for the precise value of contact area and no attempt has been made here to estimate that important quantity.

As frequency increases the retraction portion of the F-D curve observed for the matrix also looks more and more like those measured from the domains. The distance of retraction required for the tip to separate from the adhesive decreases. Release is more abrupt. With increasing sweep frequency, the maximum adhesion force also increases. In this blend the tackifier rich domains are glassy at this temperature for all of these frequencies, so the frequency dependence of the PI enriched matrix dictates changes in the overall surface performance with frequency.

The maximum penetration depth decreases and maximum stress upon loading increases with increasing frequency. The maximum penetration in the PI enriched matrix does not correspond to a maximum stress at 0.01 Hz. In that case the real contact time is about 2 s and the real stress at maximum penetration is about zero. Arendt *et al.* indicate the characteristic relaxation time of bulk PI ( $M_w$ , 300K) (taken as the time in which the response to a step change drops to 1/e times the initial response) is about 7 s at 22°C. So at this frequency of 1 Hz the matrix is modestly plasticized by a small composition of the diester.<sup>6</sup> One would like to probe the range of behavior all the way from this slow extreme to the high rate extreme in which the matrix appears glassy. However, the commercial SPM used here cannot cover the large rate range corresponding to the transition from a glassy state to flow while measuring at only one temperature.

Another limitation in performing these measurements is caused by creep of the piezo-scanner. When the

piezo is required to travel over longer distances, the final position of the piezo upon loading just before retraction depends on the rate of movement. Even though the same travel is specified, for slow movement the piezo travels slightly farther. These small differences manifest themselves in the maximum depths and stresses reached in the loading curves. In order to assess the magnitude of the effect, F-D curves (not shown) were measured on mica using the same travel and frequencies used here. When running at 0.01 Hz the maximum force seen upon loading the hard surface is about 15 nN. For a loading rate of 1 Hz this value drops to about 2 nN. Reducing the travel of the piezo eliminates this artifact, but with the portions of the PSA surface that deform markedly on retraction, reducing the travel is not possible. This limits the applicability of studies with varying frequency to qualitative comparisons.

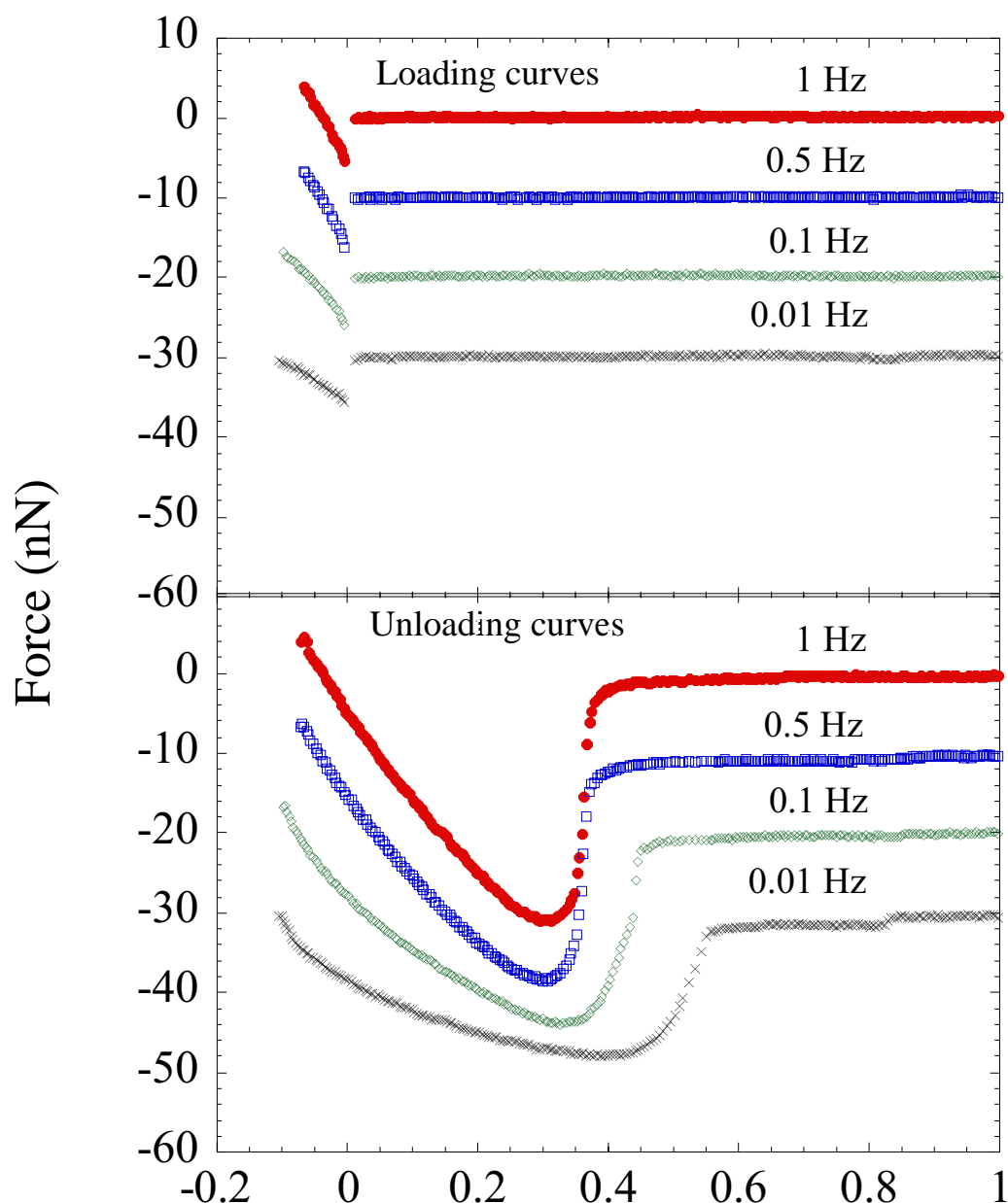


Figure 8. Force vs. distance curves taken over the frequency range of 0.01 to 1 Hz for the PI enriched matrix of the sample with 15 wt % tackifier.

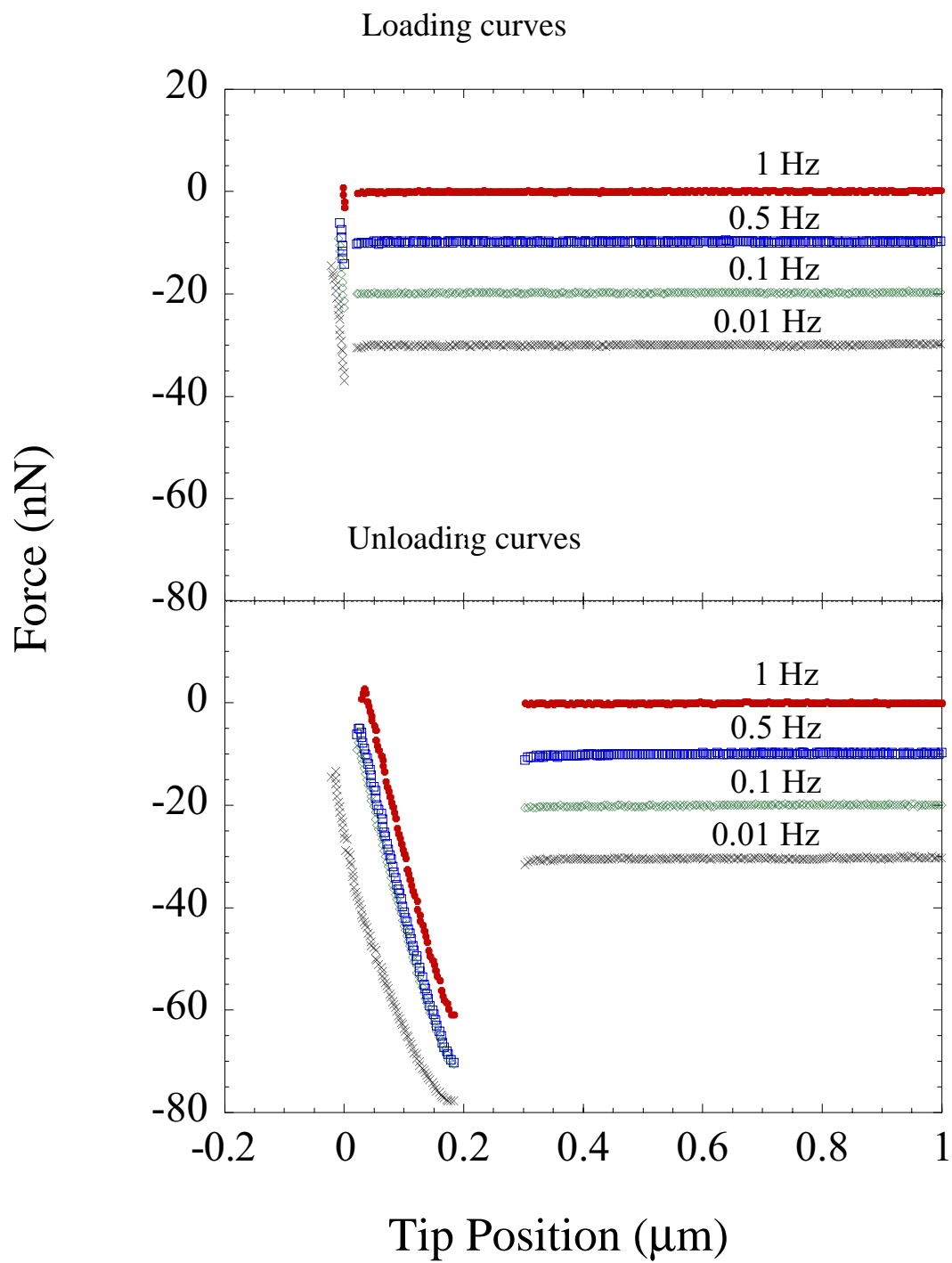


Figure 9. Force vs. distance curves taken over the frequency range of 0.01 to 1 Hz for the tackifier enriched domains of the sample with 15 wt % tackifier.

**Conclusions:** The frequency dependence of the stiffness and adhesiveness of material at the surface of a model PSA can readily be studied qualitatively in different regions on the surface using a commercial scanning probe microscope and its standard software. For the heterogeneous model blend studied here, variations in the polymer-rich matrix were predominant in determining variations in the overall surface response in the frequency range available for testing at room temperature. The behavior of the tackifier-rich domains changed very little when varying the test frequency from 0.01 to 1 Hz. At 0.01 Hz no appreciable stress is generated upon loading, indicating that the characteristic frequency of polymer segment relaxation in this case is higher than the test frequency.

### 3.) Probing Surface Mechanical Properties on the Nanoscale Using X-modulation

**Technique:** In X-modulation either the sample or tip is oscillated by sending an external voltage signal to the appropriate piezo and then three characteristics of the response are recorded: the amplitudes of in-phase and out-of-phase signals and the phase lag. Although both modulation laterally (X-modulation)<sup>7-14</sup> and modulation in the direction normal to the sample surface (Z-modulation)<sup>15-17</sup> could be used, in principle, to gain information on mechanical properties at the surface, only Z-modulation is commercially available. However, recently several research groups<sup>7,8,18</sup> have introduced X-modulation (or “locally static shear modulation mode”<sup>19</sup>) as a means to measure physical properties on the surfaces of both elastic<sup>7-10</sup> and viscoelastic<sup>11-14</sup> materials. In X-modulation, as the amplitude of oscillation is increased over a critical value the tip starts to slip and the shape of the lateral force signal with time becomes nearly rectangular. In this slip regime, the phase signal also changes. Careful attention is necessary to interpret this phase lag because it can originate from slipping of the tip, from viscoelastic deformation, or from the measurement circuitry itself. The last effect has been discussed in detail elsewhere<sup>20</sup>. Here only qualitative analysis of the X-modulation data is attempted. Quantitative analysis requires extensive calibration and evaluation of the contact area.<sup>21-24</sup> Then one must apply a contact mechanics theory using appropriate assumptions.

Important for the current study is the critical amplitude of displacement at which the transition from sticking of the tip to slipping (stick-slip transition) occurs. The magnitude of this critical amplitude is important for deciding what the origin of slip is. Whereas slip starts at very small amplitudes in the case of an elastic surface, a polymeric surface shows stick behavior even at higher amplitudes. This increase in the amplitude at which the transition occurs is associated with viscoelastic deformation. If there is any specific interaction between the tip and sample such as electrostatic, capillary, or adhesive forces, the amplitude of oscillation and magnitude of the lateral force at the transition point will also be increased. Direct observation of the stick-slip motion as a function of normal force and oscillating amplitude is a useful method to determine the strength of the adhesiveness or “stickiness” of a surface as well as the origin of the stick-slip behavior. This information is inaccessible using a commercial AFM setup.

X-modulation experiments were performed with the Autoprobe<sup>TM</sup> CP in lateral force microscopy mode using the signal access module. The sample was modulated laterally using the built-in piezo tube or an additional piezoelectric transducer (PXE-5, Philips). Driving voltage and frequency were controlled using a lock-in amplifier (SR830 DSP, Stanford Research Systems). The displacement of the sample was only a few nanometers and this amplitude was calculated after calibrating the relationship between applied voltage and piezo movement. To obtain the lateral force signal with good time definition and high accuracy, a commercial A/D converter card was installed in the computer used for data acquisition. Data on the magnitude of the lateral force could then be captured at acquisition rates of up to 250,000/sec using commercial software. A single silicon probe (Ultralever B, Park Scientific Instruments) was used for nearly all the measurements presented here. Where a different probe was used this has been noted. The oscillating lateral force signal was obtained with the z-feedback turned off, because the feedback loop could lead to deterioration of the signal quality.

All measurements were done inside a glove box under controlled relative humidity (RH) of 20% and controlled temperature (25±1 °C). For this relative humidity a contaminant layer of primarily water will be present on the sample surface.<sup>25</sup> There are two possible influences the presence of this layer may exert on the



results. First, the presence of the meniscus between the tip and contaminant layer will lead to an additional attractive force on the tip of order 6 nN. The presence of the meniscus could be eliminated by measuring under liquid, but that has not been done here. Placing the sample under any liquid environment would mean that the "interface" measured would be different than the "surface" typically present under ambient conditions. In general, an adhesive surface may be mobile and able to rearrange. This is certainly true in the present case, for which the glass transition temperature of the model adhesive blend is markedly below room temperature.

The second way in which the contaminant layer at 20% RH may influence the results is by acting to lubricate the contact between the tip and the surface. On a hydrophilic surface such as that of mica<sup>26-27</sup> the water layer present at 20% RH reduces the frictional force measured in friction loop scans. For the hydrophobic surface of a self-assembled monolayer<sup>27</sup> a complicated variation in friction with humidity has been observed.

**Sample materials and preparation:** The possibilities afforded by characterization with X-modulation can be highlighted by considering three PEP/nBEAA samples of thicknesses between 50 and 70 μm. One sample is pure PEP and the other two are blends containing 60 wt% and 80 wt% tackifier. These blends are denoted by the abbreviations PEP/60 and PEP/80. The surface of the PEP/80 sample is heterogeneous, as shown in Figure 10, displaying a morphology of tackifier enriched domains in a polymer-rich matrix<sup>28</sup>. The surface of the PEP/60 sample is homogeneous. Key to the current discussion is the observation that a microindentation test also reveals the highest work of adhesion at this composition<sup>29</sup> for which the surface is homogeneous.

**First observations on heterogeneous PSA surfaces:** In earlier work we had noted that there were real differences in the lateral force felt by the scanning tip on the domains and the matrix, as measured by LFM. Variations in topography can, though, cause apparent differences in friction that are not real, but contrast reversal between an image scanned left-to-right (LR) and that scanned right-to-left (RL) was offered as evidence that these lateral force differences were real. This reversal is also seen in lateral force images, shown in Figures 10a,b, that were obtained more recently on the same sample. It has been pointed out<sup>18</sup> that a more rigorous approach to discriminating against topographical artifacts is to consider the difference image created by subtracting the RL image from the LR image. Such a difference image is presented in Figure 10c. It is clear that qualitative differences between lateral force on the domains and in the matrix remain after this further treatment of the image. A trace of lateral force as a function of position along the line shown in Figures 10a,b is shown in Figure 10d. The trace shows the lateral force being higher in the matrix for both scanning directions and also when measuring with two different microscopes (CP and Explorer). Further study with X-modulation measurements reveals that the higher lateral force seen in the conventional lateral force scan is not necessarily indicative of higher adhesiveness in that region of the surface.

**Stick-slip transition:** Measurements were made first on an elastic silicon wafer in order to understand the general features of the measurement approach with a system in which there is no viscoelastic behavior. Selected results from these measurements are presented in Figures 11a,b to introduce the key features of the data. For the silicon wafer surface, upon which there is a native oxide layer of about 15 Å thickness, a stick-slip transition is seen as the amplitude of oscillation is increased from 0.02 V (Fig. 11a) to 0.04 V (Fig. 11b). This is demonstrated in Figures 11a,b which show the variation in LFM signal with change in maximum displacement. For a small displacement corresponding to 0.01 V input voltage the shape of the LFM response indicates a "stick" behavior. The response is sinusoidal. An amplitude of 0.01 V corresponds to a lateral displacement of 2 nm and 0.1 V corresponds to 20 nm. When the amplitude of displacement is increased by a factor of four and then ten, the shape of the response changes markedly. In Figure 3b, on the left side of the trace, when the tip is passing through the position associated with "zero" lateral displacement, the shape of the response tracks that of the input. The tip "sticks". As the displacement increases the response changes shape. The plateau in the LFM signal is caused by "slip" between the tip and surface.<sup>10,30</sup> With increasing forcing amplitude, the peak-to-peak amplitude of the response increases in the stick regime because the extent of cantilever torsion is directly proportional to the sample displacement. When the lateral force exceeds the static friction, the tip starts to slip and then the lateral force reaches a constant value. This constant value is the so-called dynamic friction force, which corresponds to one half the peak-to-peak amplitude. Since the interaction between the tip and the silicon oxide surface is purely an elastic contact, we cannot observe the static barrier at the transition region.<sup>31</sup> One of

the important features of the slip regime is that the peak-to-peak response decreases with increasing forcing amplitude. The same behavior has also been seen with a second elastic surface, mica.<sup>11</sup>

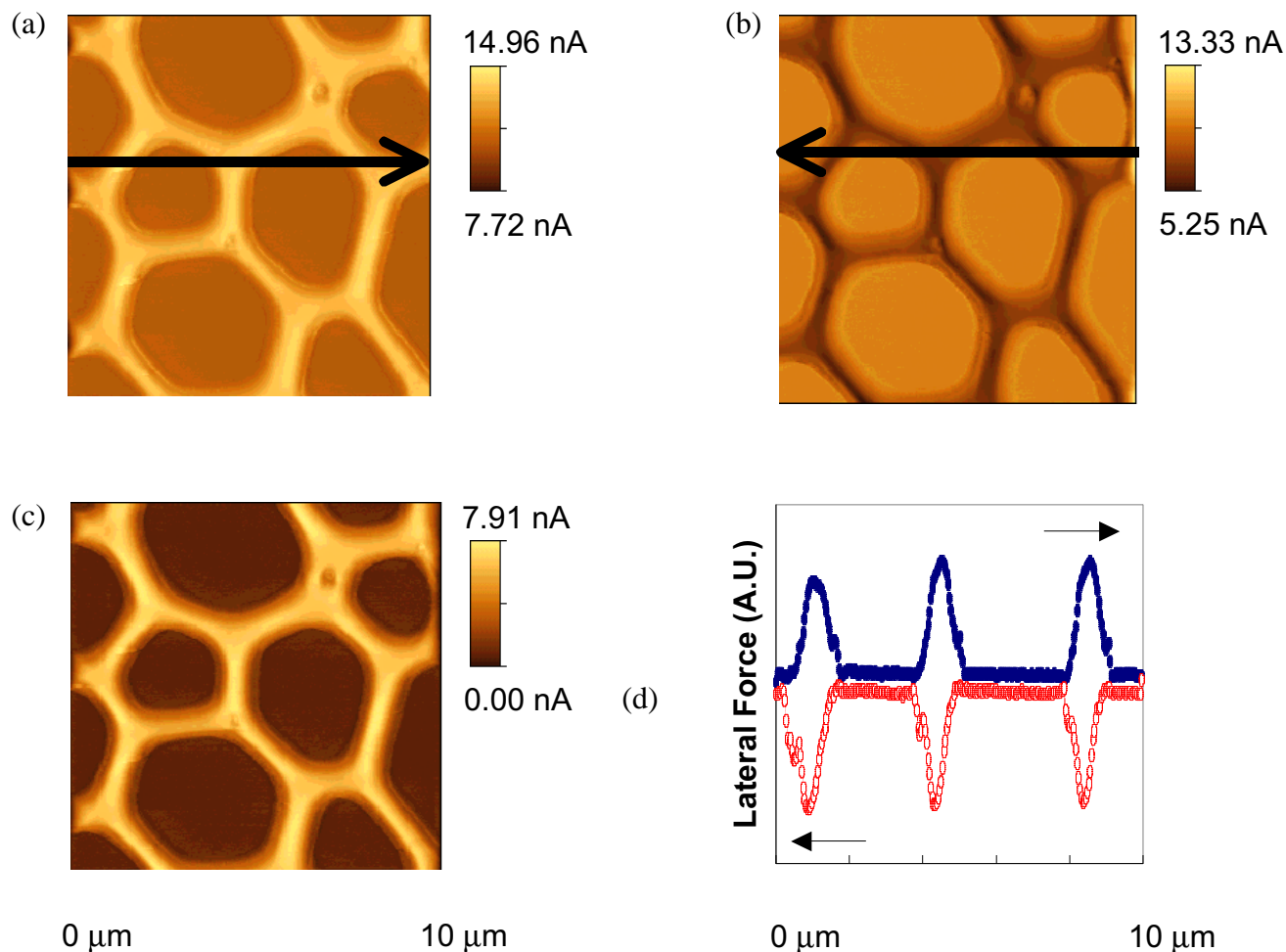


Figure 10. Scanning probe images of the PEP/80 sample presented using the standard output of a commercial software package: (a) LFM image, scanned left to right (LR). (b) LFM image, scanned right to left (RL). (c) Difference image (LR – RL). (d) Trace of the variation in LFM signal amplitude along the line shown in images (a) and (b).

The various surfaces studied here showed different stick-slip behaviors. The X-modulation responses of the matrix and domains of PEP/80 were sharply different. The response of the matrix, shown in Figure 11c, was sinusoidal and the peak-to-peak amplitude increased monotonically with forcing amplitude for the entire range of forcing amplitude investigated. By contrast, in the domains slip was observed at sufficiently high values of forcing amplitude, as shown in Figure 11d. The shape of the response in the slip regime was not symmetric as it was for the silicon oxide surface, but a plateau region and peak-to-peak amplitude could still be defined. The origin of this asymmetry is not yet clear. The peak-to-peak amplitude did decrease with increasing forcing amplitude for the domain regions in the slip regime, just as it did on silicon oxide. The significance of the differences between the behaviors of the matrix and domains will be discussed below.

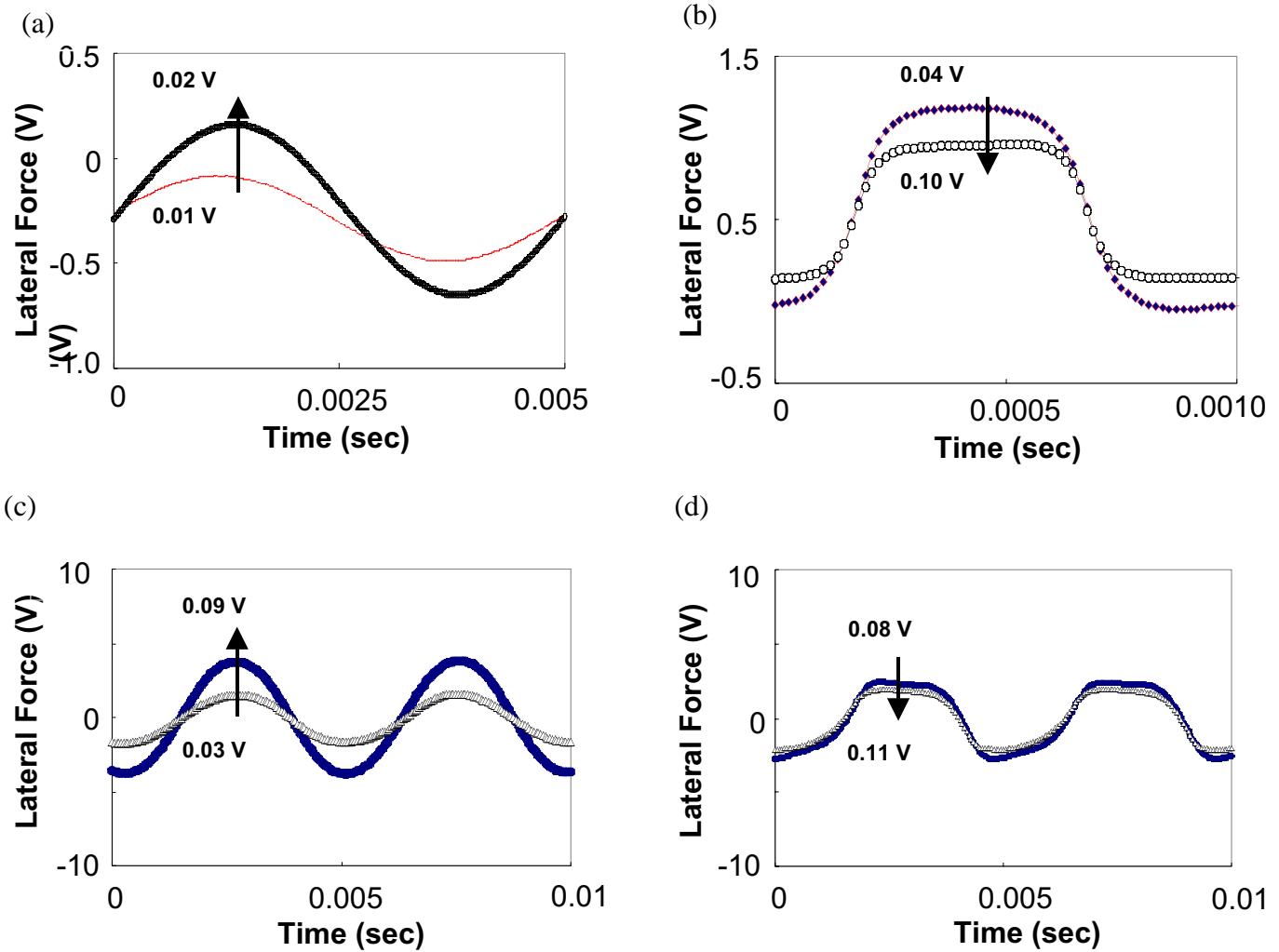


Figure 11. Characteristics of stick-slip motion. The uncalibrated lateral force response as a function of time: (a) stick regime of silicon oxide (200 Hz, 1 nN) and (b) slip regime of silicon oxide (1 kHz, 3 nN). The amplitude of the forcing function is shown in volts for each curve. Note that the lateral force increases or decreases with forcing amplitude depending on the regime. The uncalibrated lateral force response as a function of time is also shown for (c) the matrix of PEP/80 (200 Hz, 1 nN), and (d) domain of PEP-80 (200 Hz, 1 nN).

**Normal force effect on X-modulation:** Since increasing the normal force increases the static friction, the LFM signal increases with normal force, as one would expect for a single asperity contact. The stick-slip transition of silicon oxide also occurs at a higher forcing amplitude with increasing normal force, as shown in Figure 12a. The transition occurs at a forcing amplitude of around 0.02 V under high normal force (10 nN), but slip occurs at a forcing amplitude below 0.02 V under a lower normal force of 1 nN. Note that there is no appreciable hysteresis in the voltage sweep.

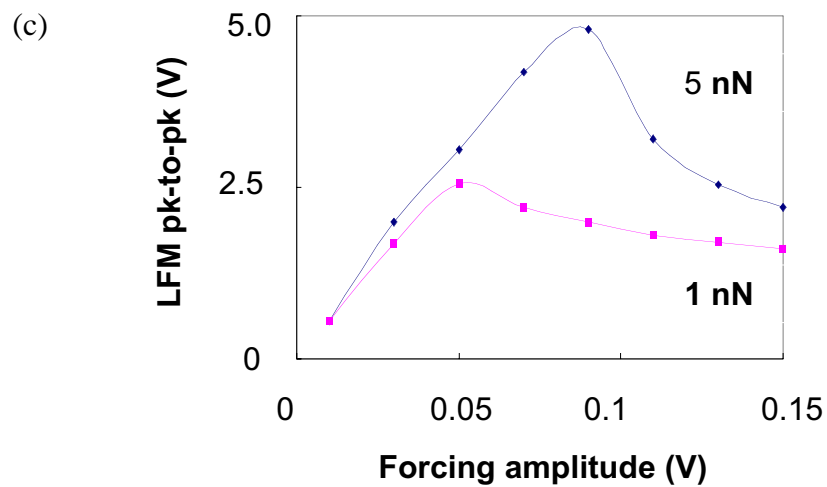
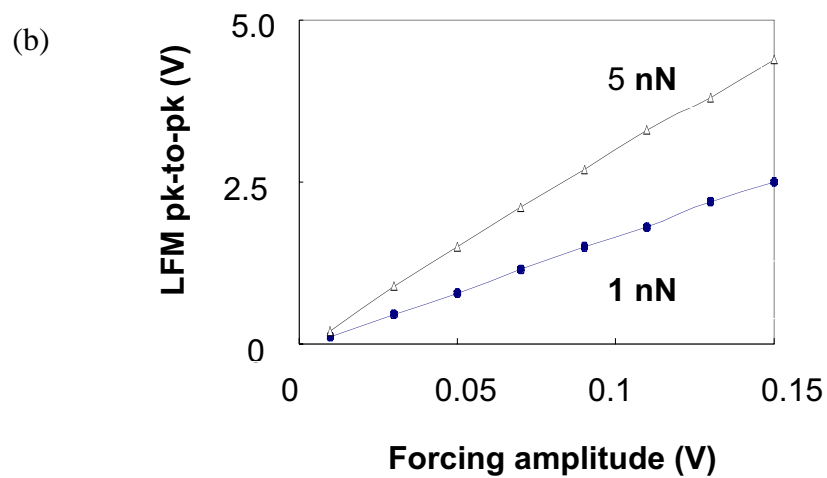
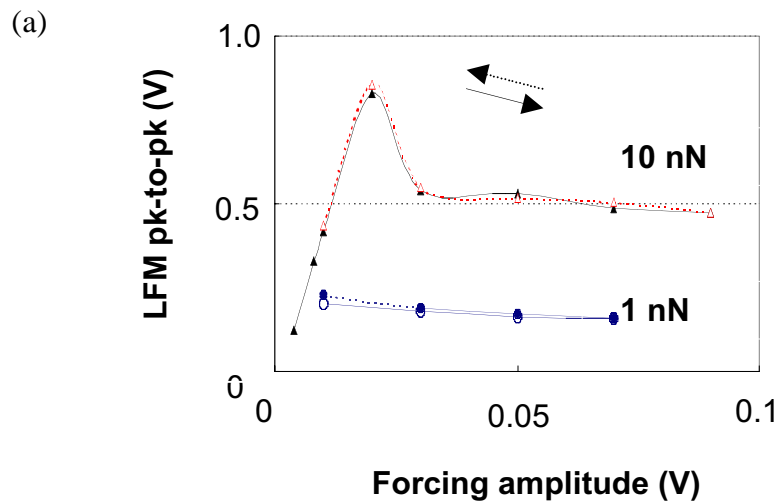


Figure 12. Effect of normal force on the stick-slip transition for X-modulation at 200Hz on: (a) silicon oxide (b) the matrix of PEP/80, and (c) the domain of PEP/80.

Figure 12b shows how the LFM signal of the matrix of PEP/80 increases with normal force. All the response signals were sinusoidal and no slip occurred within the range of forcing amplitude experimentally accessible. A similar normal force effect can be seen in the domains of PEP/80, as shown in Figure 12c. The fact that the forcing amplitude and peak-to-peak LFM signal at which the stick-slip transition occurs strongly depend on the normal force can be used to evaluate the stickiness of the adhesive surface.

A special behavior was also observed around the frequency of 700 Hz, which is a resonant frequency of the piezo. At that frequency the peak-to-peak response increases with increasing piezo driving voltage. Near this frequency, for a given input voltage, the lateral displacement of the cantilever is larger than at other frequencies. This frequency effect has not yet been probed, but should be in the future, since the frequency dependence of the rheological properties of a polymer surface is important.

*Evaluation of stickiness of an adhesive surfaces.* Before discussing the results we consider the verification of the accuracy and reliability of the modulated signal. As mentioned earlier, the z-feedback can interfere with the acquisition of the oscillating LFM signal in X-modulation. Although the amplitudes of the oscillating A-B and LFM signals generated by the z-feedback are relatively small, they are large enough to obscure the sinusoidal output signal for small sample displacements where the amplitude of LFM signal from the feedback is comparable to that of the modulated LFM signal.

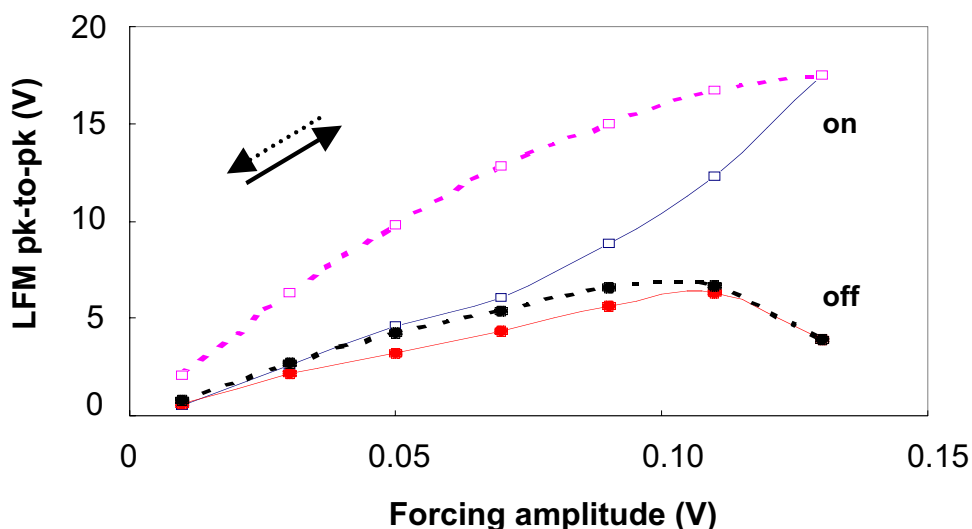


Figure 13. Hysteresis in lateral force during sweeps of forcing amplitude under 5nN normal force with feedback on for PEP/60.

Figure 13 presents the peak-to-peak amplitudes of the oscillating LFM signals on the PEP/60 sample obtained while first increasing and then decreasing the driving voltage with feedback on. There is a large hysteresis during the voltage sweep for both the PEP/60 sample and for the domains of PEP/80 (not shown). However, the data for the matrix (not shown) show little hysteresis and the data for PEP (not shown) show no hysteresis at all. As mentioned before in connection with Figure 12a, the data for the silicon oxide surface also show no hysteresis. (Note that the voltage scale in Figure 12a has units of mV.) The extent of hysteresis may be related with the strength of the surface stickiness, because strong interaction between the tip and sample can deform the surface seriously during feedback operation. When the feedback was turned off, this hysteresis was reduced remarkably and the stick-slip transition became observable.

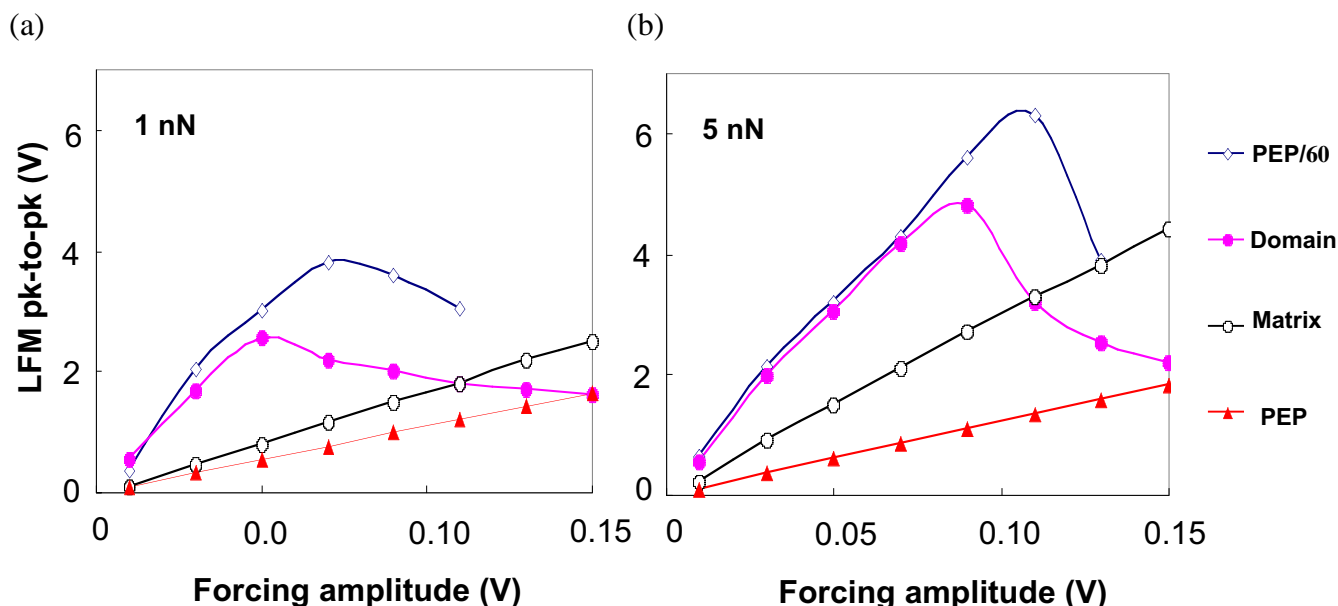


Figure 14. Comparison of the changes in the peak-to-peak lateral force signal with forcing amplitude at 200 Hz with z-feedback off and following an ascending voltage sweep with normal force of (a) 1nN or (b) 5nN. Note that magnitudes of the lateral forces differ somewhat with those shown in Figure 3c,d, because the data shown in Figures 3c,d were taken with a different cantilever.

Figure 14 presents data showing the differences in behavior among the four surfaces studied. All the data were obtained with z-feedback off while sweeping the driving voltage rapidly in the ascending direction using exactly the same tip. For the PEP and matrix surfaces, only "stick" behavior is seen no matter what normal load or frequency (not shown) is used in the range of amplitude of X-modulation available here. The response is sinusoidal and the peak-to-peak amplitude monotonically increases with forcing amplitude. This behavior results from the viscoelastic nature of the surface. The peak-to-peak response for the matrix is higher than that for PEP at both values of normal force, 1nN and 5nN. This is expected because the matrix contains some tackifier. In the "bulk" of the sample the tackifier concentration in the matrix must be lower than the overall tackifier loading (80 wt%). However, the surface of the matrix is almost certainly enriched in tackifier as compared to the bulk matrix. Exactly how high the concentration of tackifier is in the "matrix" phase at the surface is a key, but as yet unanswered, question.

The surfaces of the domains and the PEP/60 sample showed behaviors sharply different from those of PEP and the matrix. When the properties of the domain were probed, a "stick-slip" transition was observed at a forcing amplitude of 0.05 V under 1nN load and at 0.09 V under a normal force of 5nN. Above these critical voltages the shape of the response changed from sinusoidal to nearly rectangular and the peak-to-peak response amplitude started to decrease with increasing forcing amplitude. These transitions occurred at much higher forcing amplitudes than in the case of the silicon oxide surface (Figure 12a). Also the lateral force in the stick regime was much higher for the domains and PEP/60 than for silicon oxide, PEP, or the matrix. From the higher transition amplitude and lateral force, as well as the presence of the stick-slip transition itself, we conclude that the domain has both elastic and sticky characteristics. The data from the PEP/60 sample show similar trends to those seen for the domain, but the transition amplitude and lateral force in the slip regime are higher for PEP/60. The surface of the PEP/60 sample must be uniformly enriched in tackifier to a composition that is similar to, but probably less than, the tackifier surface composition in the domains of the PEP/80 sample.

The silicon oxide surface is hard enough so that the tip truly sits on the surface under the loads used here. However, one expects that there is some penetration into the other four surfaces. F-d curves have demonstrated that the matrix is softer than the domains<sup>5</sup> and thus the penetration into the matrix is greater. The amount of penetration will also depend on dwell time, as shown by Basire and Frétny,<sup>13</sup> who measured



stiction curves for a "styrene-butadiene copolymer" after varying amounts of dwell time. For all the data here the dwell time before initiation of the X-modulation was kept short (less than 15 seconds), though not rigorously constant.

For x-displacements approaching zero all surfaces display stick behavior. For the silicon oxide surface the slip occurs already for relatively small forcing amplitudes. For the PEP and matrix, stick is always seen. The behaviors of the tackifier-enriched domain and PEP/60 are more complex. For small displacements the adhesive nature of the domains is important, leading to a lateral force response that is markedly higher than that on silicon, PEP, and the matrix of PEP/80. Above this transition value of displacement the fact that the domain and PEP are "sticky", as proven by F-d measurements, becomes less important.

Here, finally, we have our explanation of why the lateral force is higher in the matrix regions when performing conventional LFM measurements on the adhesive blend. ***Lateral force measured in the large scale scans corresponding to "lateral force imaging" are not appropriate for determining what portion of the surface is "sticky".*** The lateral forces in the LFM scanning images are dominated by deformation effects, not by variations in the adhesive character of the surface. The deformation of the surface in response to the rastering tip is larger in the matrix, leading to a larger torque on the cantilever when the tip is on the matrix than when the tip is on the domain. This torque has its origin in the viscoelastic properties of the matrix, not its "stickiness". It is the domain that is actually "stickier." This is a reason why "adhesive force" mapping of surfaces has an appeal when one is seeking to discover which portions of the surface are more highly adhesive. However, as emphasized above, such measurements do not necessarily truly probe the surface behavior. Therefore small amplitude X-modulation measurements are preferable for looking at surface adhesive character.

**Conclusions:** X-modulation was applied to the characterization of the surface mechanical properties of a PSA blend for the first time using the PEP/nBEAA system as an example. The measurement of lateral force in response to small amplitude lateral oscillations of the sample (X-modulation) proved to be an effective means of identifying key qualitative differences in the nanomechanical behavior of adhesive surfaces. The technique itself has recently been developed by others, but was applied to the study of PSAs for the first time by us. The characteristic features of "stickiness" and elasticity manifest themselves in the presence or absence of a "stick-slip" transition and changes in the forcing amplitude at which this transition takes place. While conventional lateral force microscopy imaging of a heterogeneous PSA surface leaves the impression that the polymer-rich matrix regions are responsible for the adhesiveness of the surface, X-modulation measurements make it clear that the tackifier-enriched domains provide the adhesiveness. X-modulation measurements also indicate that the homogeneous surface of the adhesive loaded with 60 wt % tackifier is more "sticky" than the more adhesive domains in a heterogeneous surface of a PSA with higher tackifier loading. The tackifier loading (60 wt %) giving the best overall performance as indicated by microindentation, which is sensitive to bulk rheology, also corresponds to the best adhesiveness right at the surface of the adhesive for this system.

#### **4.) Detection of surface segregation due to molecular weight alone using x-modulation**

The measurement of x-modulation at the surface of a film should provide a means by which one can identify, and potentially quantify, the segregation of a low molecular weight species to that surface. While a tackifier is a very important example of such a low molecular weight species that can migrate to a surface, we have also considered a model polymer blend in which the only difference between the two components is molecular weight. Molecular weight driven segregation in polystyrene blends has already been studied with other techniques, which, however, require the use of isotopic labeling in order to measure the concentration depth profile. ***No method of sensing molecular weight driven surface segregation without labeling has yet been published in the open literature.***

X-modulation experiments were performed with the Autoprobe™ CP in lateral force microscopy mode using the signal access module. The sample was modulated laterally using the built-in piezo tube or an additional piezoelectric transducer (PXE-5, Philips). The output signal was analyzed using a lock-in amplifier (Stanford Research Systems, SR830 DSP). The quantity of interest was the peak-to-peak voltage corresponding to the lateral force exerted on the cantilever when the sample was modulated in the x-direction with a given amplitude.

Initial measurements with blends of polybutadiene (PB), which are closely related to adhesive products of practical interest met with difficulties due to the speed with which the PB surface is damaged by lateral modulation of the tip at room temperature when the polymer is very soft. With the original technique as much as 20 minutes was required to obtain a data set of interest and this proved impractical. Therefore blends of high molecular weight (890,000 g/mole) and low molecular weight (11,400 g/mole) polystyrene (PS) standards were investigated. (In future work the short acquisition time required with the new automated protocol should make it possible to study even "soft" systems.) Films for study were spun cast onto silicon wafers. *A key finding was that sample thickness has to be greater than about 200 nm to prevent the presence of the high modulus substrate underneath the film.*

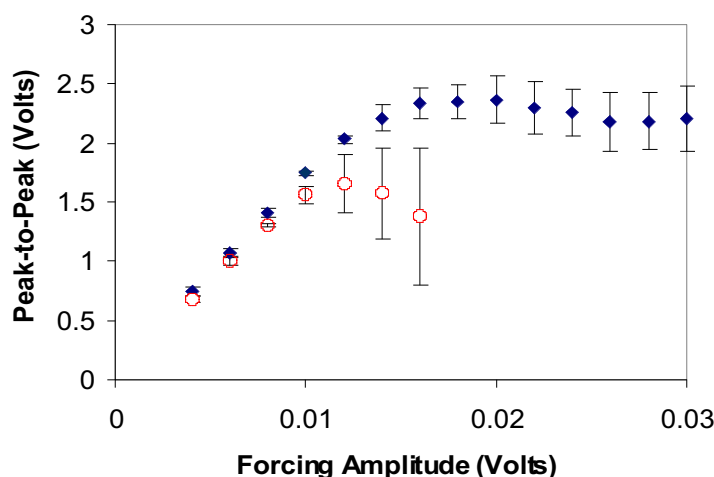


Figure 15. Preliminary data for the lateral x-modulation force (expressed as peak-to-peak voltage) as a function of modulation amplitude (expressed in volts) for two polystyrene films of molecular weight 890,000 g/mole (circles) and 11,400 g/mole (diamonds). Their behaviors are clearly distinguishable in the "slip" region.

Once the proper sample preparation was defined, samples of three kinds were made: 1.) pure low molecular weight PS, 2.) pure high molecular weight PS, and 3.) blends of the two molecular weights. In Figure 15 we present data from the single component films. Shown are the peak-to-peak lateral force responses as a function of amplitude of the x-modulation movement. That is, a sample was oscillated with different amplitudes and the response of the tip was monitored for each case. Both the response, which is a lateral force, and the driving amplitude are reported simply in volts. The driving amplitude has been calibrated. A forcing amplitude of 0.01V corresponds to an lateral amplitude of 2 nm. The lateral force has not yet been calibrated. One sees that the peak-to-peak lateral force increases linearly with driving amplitude initially for both samples. This first region of the response corresponds to a "stick" behavior in which the tip is twisted as the sample is translated. Contact between the tip and sample are maintained. At higher forcing amplitude the tip begins to slip on the surface. When this occurs, the lateral force begins to level off or drop. The behavior of the two samples are clearly distinguishable, giving us reason to believe that it should be possible to distinguish surface enrichment for some blends. Of course the success with which surface enrichment may be recognized will depend upon how different the rheological or mechanical behaviors are for the two components of the blend.

Initial results obtained by a summer undergraduate researcher indicated that for sufficiently thick films, measurements of a *blend* did suggest that the surface nanomechanical properties were consistent with the presence of some considerable amount of lower molecular weight material at the surface. However, the student obtained only an incomplete set of data on films of proper thickness before leaving. Due to the sizes of the uncertainties in the data and gaps in the series of samples for which good data sets were obtained, it has not yet been possible to draw conclusions about the concentration of the lower molecular weight species segregated to the surface of a blend sample.

**Conclusions:** The mechanical properties of the surfaces of two polymer films in which the chains have identical chemistry, but markedly different molecular weights, can be resolved by X-modulation measurements. First results suggest that the segregation of a low molecular weight material to a polymer/additive blend surface may be distinguished by X-modulation.

## 5.) Studying Humidity Effects with X-modulation

**Experimental:** To minimize hysteresis effects, we collected each entire data set within 30-40 secs, a rate 4-5 times faster than that used earlier for the X-modulation experiments presented above<sup>32</sup>. The faster data acquisition was made possible using computer-assisted measurement automation. A high speed commercial D/A (Digital to Analog) conversion card was installed in the computer and it was controlled by way of the commercial software package, LabVIEW™.

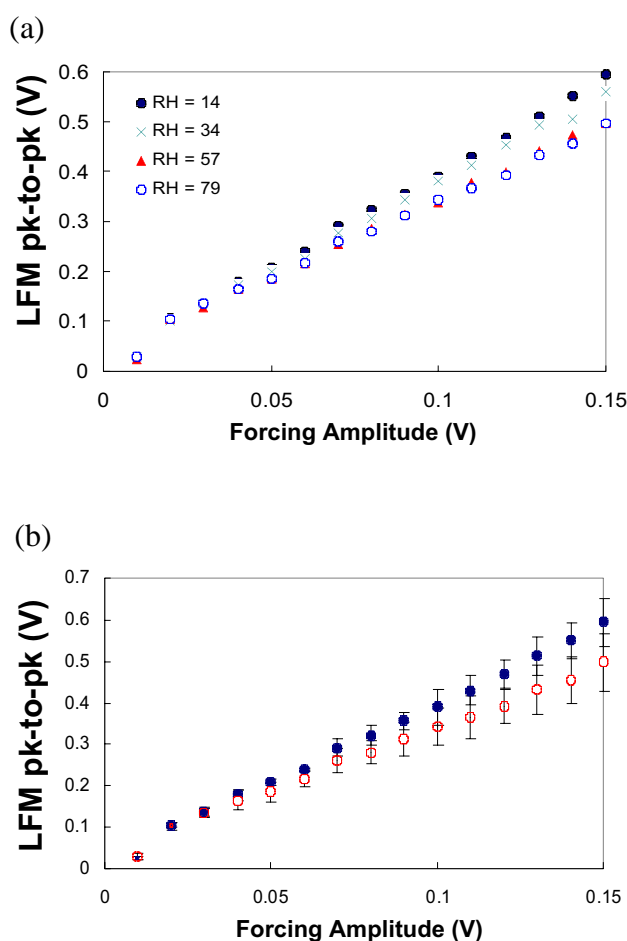


Figure 16. Effect of humidity on lateral force at PEP surface using normal X-modulation at 200Hz : (a) average value (n=5) of peak-to-peak lateral force at four different humidities as indicated in the legend, (b) data at the lowest (RH=14 %) and highest (RH=79%) humidity shown with uncertainties corresponding to one standard deviation.

**Results:** Figure 16a presents the peak-to-peak amplitude of the oscillating LFM signal from the PEP sample obtained at four different humidities while increasing the forcing amplitude with the z-feedback turned off. Five different positions were examined and only stick behavior was seen. Even though the magnitude of the measurement uncertainty gradually increases with increasing forcing amplitude, as shown in Figure 16b, when considering the data for the extreme values of relative humidity one recognizes that there is a slight decrease in lateral force on the PEP surface with increasing humidity. The surface of the PEP-60 sample exhibited behavior sharply different from that of the PEP surface, as shown in Figure 17. At the lower humidity, a maximum in the curve marks a transition from stick to slip behavior with increasing forcing amplitude. At higher humidity stick behavior was seen, on average, over the entire range of forcing amplitude, and the lateral force was enhanced relative to that at low humidity.

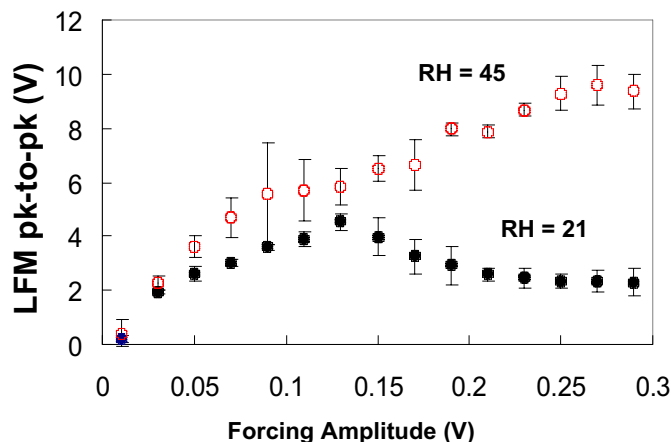


Figure 17. Variation of lateral force with forcing amplitude on the PEP/60 surface measured using normal X-modulation at 200Hz and two relative humidities, 45% (○) and 21 % (●).

The results presented in Figures 16 and 17 differ in some ways from those for other sorts of surfaces reported already by others. In discussing our results it is helpful to consider if the arguments developed by others are appropriate to our system. It has been reported that for hydrophilic surfaces such as mica,<sup>33</sup> silicon oxide,<sup>34</sup> and an MoS<sub>2</sub> single layer on mica<sup>35</sup>, the friction or the friction coefficient decreases with increasing RH at high humidity (over 60~70% RH). The rationale given for this behavior has been that water serves as a boundary lubricant in the contact region in these cases. This trend becomes less important for hydrophobic surfaces, apparently because the water molecules are unable to penetrate the contact junction. A different behavior is observed for hydrophilic surfaces<sup>35</sup> at low humidity. At low humidity either no special effect is observed<sup>3</sup> or the friction coefficient increases with increasing RH.<sup>35</sup> The authors of the study in which this behavior has been reported<sup>35</sup> argue that the behavior is related to the presence of an increased capillary force at higher RH. The increased attraction of the tip for the surface would increase the force necessary to move the surface relative to the tip, i.e. the shear force. Even if the details of the explanations vary slightly among papers, most of the arguments share a common characteristic. They are based mainly on the discussion of changes in capillary force with humidity. In general, there is a discontinuous change in the capillary force at low relative humidity between 20 and 40%, depending on the nature of the solid surface. Beyond the transition point, there is not much agreement on the trend. Salmeron and co-workers<sup>36</sup> and Overney and co-workers<sup>37</sup> have observed the capillary force decreasing above the transition point (~ 40% RH). However, their explanations are quite different. While the former group argues this behavior is due to a simple effect of tip geometry, the latter group proposes a mechanism involving an enhancement of the repulsive force through chemical bonding of the

liquid in the gap. This argument is based on earlier results of Mate and co-workers.<sup>34</sup> However, in some other studies the capillary force is seen to increase gradually with humidity.<sup>38,39</sup>

The implication of the above discussion is that the effect of water is much more complex than had been previously suspected, a point discussed well by Piner and Mirkin.<sup>40</sup> Moreover, in the case of soft materials, understanding the effect of humidity becomes more difficult due to the presence of surface roughness and deformation of the surface during contact. For example, the hydrophobic surface of a self-assembled monolayer<sup>41</sup> shows a complicated variation in friction with humidity. Thus, attempts to describe our observations simply by drawing connections between the capillary force and relative humidity will probably not be satisfactory.

Another important question is whether our results obtained using X-modulation are comparable to macroscopic data such as values of a macroscopic sliding friction coefficient. Friction measurements on a macroscopic scale are usually used to define the friction coefficient as the ratio of the friction force to normal load, and the friction force is obtained using friction loop scans. As mentioned earlier, surface stickiness itself can be manifested in X-modulation, which is of course the most important parameter for the study of adhesive surfaces. However, surface stickiness becomes much less significant in macroscopic friction measurements due to the role of surface deformation. Under the conditions for macroscopic measurements, the velocity of the tip is sufficiently high to overcome the tendency for the tip to stick to the surface. Both the contact area and the contact time at any point on the surface are reduced relative to an X-modulation measurement.

**Conclusions:** Using the X-modulation technique one can probe the effect of humidity on adhesion at the surface of a polymer matrix and a model adhesive containing tackifier. While the oscillating lateral force on the surface in the "stick" regime decreases slightly with increasing humidity on the hydrophobic PEP surface, it increases strongly with humidity on the homogeneous surface of the adhesive loaded with 60 wt% tackifier (PEP/60). For the hydrophobic surface, a thin water layer may be acting as a lubricant, reducing the frictional force during tip oscillation. We explain the behavior of the PEP/60 surface by conjecturing that the PEP/60 sample has a tackifier-enriched, sticky surface with a more hydrophilic nature. This hypothesis can be tested using a force-distance measurement (F-d) during X-modulation.

## **6.) Characterization of Surfaces using X-modulation Combined with a Force-distance Measurement**

The X-modulation technique can be usefully extended by combining it with a simultaneous measurement of the force-distance curve, because in this way several pieces of information can be obtained simultaneously<sup>11,42</sup>. While the adhesive force and apparent stiffness of the surface can be estimated by analyzing the response of the cantilever in the z-direction, analysis of the lateral response provides information on the frictional behavior and the phase lag that originates from slipping of the tip or the viscoelastic properties of the sample. A schematic of the apparatus used for the X-modulation measurements combined with force-distance curves is shown in Figure 18. The sample was modulated laterally at a frequency of 200 Hz with an amplitude of 2 to 20 nm at a linear velocity of 800-8000 nm/sec using the built-in piezo tube controlled by the lock-in amplifier. Simultaneously, the sample was moved vertically toward and then away from the tip at a rate of 10-300 nm/sec. The response of the cantilever to this movement of the sample is registered by monitoring the reflection of a laser beam from the back of the cantilever and into a four quadrant detector. Vertical deflection of the cantilever is quantified to deduce the normal force on the cantilever, while the lateral force at the sample surface is derived from the twisting of the cantilever. To obtain the A-B and lateral force signals with good time definition and high precision, a commercial A/D converter card was installed in the computer used for data acquisition. To obtain more specific information such as the amplitude of oscillation and phase lag of the lateral response, the lateral force signal was passed through the lock-in amplifier and then the processed signals were fed to the data acquisition software.

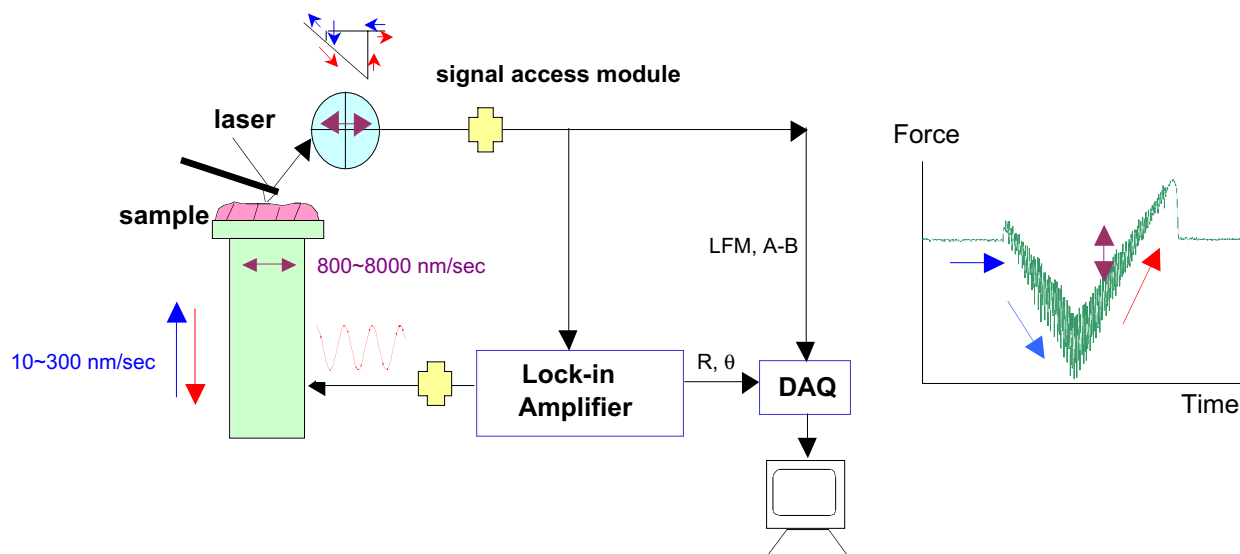


Figure 18. Schematic of the instrumentation used for characterization of the surface by X-modulation with simultaneous collection of a force-distance curve. To the right is shown also the variation of the LFM signal as a function of time for this type of measurement.

Data acquired during relatively fast loading (360 nm/sec) with X-modulation at 200Hz are shown in Figure 19. Four signals were captured simultaneously over a 1 second period. Vertical deflection of the cantilever (as registered in the A-B signal) is quantified to deduce the normal force on the cantilever, while the rms lateral force,  $R (= \sqrt{X^2 + Y^2})$ , at the sample surface is derived from the twisting of the cantilever, where X and Y correspond to the in-phase and out-of-phase amplitudes, respectively. The average uncalibrated lateral force (expressed in volts) is calculated as

$$F = 0.5(\text{Peak-to-peak amplitude}) = \sqrt{2} \bullet \sqrt{X^2 + Y^2}$$

and the phase angle is given by  $\tan^{-1}(Y/X)$ .

The lateral modulation of the sample manifests itself in the high frequency oscillations seen superposed on the force vs. time curve (marked "LFM") which is an analog of a more conventional force-distance curve. On the left side of the graph the trace corresponds to the approach of the sample to the tip before contact. The tip jumps into contact with the sample at the point where the force suddenly increases. Then the curve begins to move down. This corresponds to the increase in normal force as the tip penetrates into the sample. So the slope of this curve is determined by the rate of the z-modulation and the compliance of the material, the slope increasing with decreasing compliance if the compliance of the sample is less than that of the cantilever. The lowest point in the curve marked "LFM" corresponds to the end of the loading process and beginning of the unloading process. For this sample we find that the unloading also results in a linear force vs. time trace, but the trace rises above the zero force level, which means that the tip adheres for some time to the surface. Once the force attempting to restore the cantilever to its rest position exceeds the adhesion force, the tip snaps off the surface and the force returns to the same value (zero) as before contact. Although the oscillations of the LFM signal can be recorded clearly for a high loading speed experiment, the processed signal, R, shows a delay which is an artifact of the limited acquisition speed, which makes it difficult to analyze the results precisely.



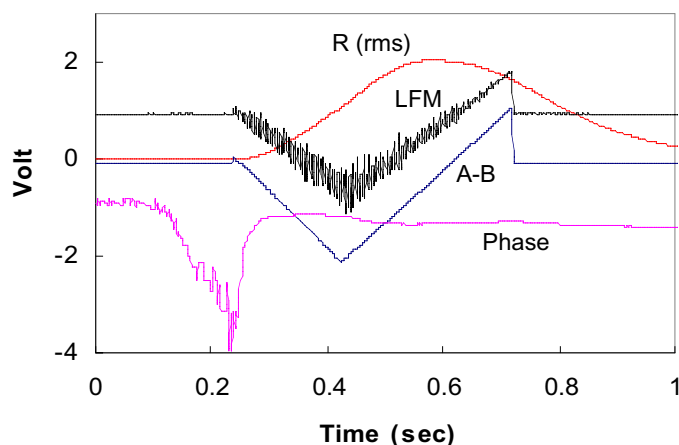


Figure 19. Traces vs. time of four signals captured simultaneously during a measurement combining X-modulation with a force-distance measurement with a fast loading rate (360 nm/sec). The signal marked “R” is the rms lateral force corresponding to the magnitude of oscillating lateral force (LFM). The “A-B” signal is related to the vertical deflection of the cantilever. “Phase” is the phase difference between the input and output signal. The “LFM” signal is the lateral force signal.

If one is willing to sacrifice resolution of the detail in the oscillating LFM signal, artifact-free processed signals can be captured by reducing the loading speed to 10 nm/sec. An Ultralever™ B cantilever (normal spring constant = 0.4 N/m) was used in this experiment with a forcing amplitude of 0.004V, which corresponds to a lateral displacement of the sample of 0.8nm to keep the tip in the stick regime during acquisition. Once slip occurs, the response is controlled by slip phenomena and the challenges in determining the surface properties from the data become even greater. Four different surfaces were studied. The first was the hard, elastic surface presented by the native oxide of a silicon wafer. A second elastic surface was that of a glassy polystyrene (PS) film. The third surface was that of poly(ethylene propylene) (PEP). This homopolymer has been used as the matrix in the model adhesive. Finally, the aged PEP/60 sample was studied. This particular composition blend has been found to be the most highly adhesive as noted above.<sup>28,32</sup> The responses, summarized in Table 2, were sharply different among the different samples.

**Table 2. Variation in Properties of PS, PEP, and PEP/60 Surface.**

	Experimental conditions			Results		
	RH (%)	Temperature (°C)	Forcing Amp. (V)	Stiffness (nN/nm)	$\theta_{\max}$ (deg)	<b>R</b> normalized ( $V_{\text{rms}}$ )
PS	23	24	0.004	0.30	0.7	0.4
PEP	23	24	0.004	0.073	13.7	0.1
			0.05	0.066	10.3	1.3
			0.1	0.065	9.8	2.5
	77	25	0.004	0.074	13.4	0.1
			0.05	0.066	10.4	1.0
			0.1	0.061	9.9	2.1
PEP/60	23	24	0.004	0.21	0.8	3.2
	40	24	0.004	0.14	1.0	5.7
	77	25	0.004	0.06	3.5	23

Before discussing differences among the surfaces, three important points should be considered. First, even though the silicon wafer was selected as a type of reference sample, the results from that surface can not be compared directly with those from the other surfaces because the behavior was of the “slip” sort, even for this smallest displacement. The high value of the phase lag ( $\theta \sim 20^\circ$ ) is clear evidences of the slip occurring. When slip occurs, the slope of the loading curve decreases with increasing tip deflection in the force distance curve<sup>43</sup> and a finite phase lag will be observed, even though the material is elastic.<sup>30</sup> Therefore, we used PS as a reference sample for further discussion. Since  $R$  is a function of normal force, if the final load force,  $F_{n,max}$  varies among samples, that variation has to be accounted for before comparing values of  $R$  among samples. Here, we compare values of  $R_{reduced}$  ( $=R_{max}/F_{max}$ ), rather than using values of  $R_{max}$ , where  $R_{max}$  is the uncalibrated lateral rms force at the maximum load,  $F_{max}$ .

Finally, we have to consider the reliability of a force-distance experiment using AFM as a tool for nanoindentation. An overview of nanoindentation measurements of polymers has been provided by VanLandingham.<sup>44</sup> The advantage of using a commercial AFM instrument for such a measurement is the potential to combine nanoindentation with high resolution imaging capability. However, because commercial AFM systems have not been specifically designed for indentation testing, a number of instrumental uncertainties severely limit their uses as nanoindentors. Despite these limitations, successful studies of polymers have been completed by either reporting the results on a relative basis or by reporting them with large uncertainties due to the use of nominal spring constants, the assumption of idealized tip shapes inherent to the Hertzian<sup>45</sup> or Sneddon<sup>46</sup> analysis, and the neglect of viscoelastic behavior. This assessment is exactly applicable to X-modulation. Obtaining reliable quantitative results requires calibration of all the parameters with high accuracy. However, this calibration is a non-trivial process having much higher uncertainty than for nanoindentation. Therefore, we first focus on qualitative and relative comparisons among the different surfaces. However, we have tried to calculate penetration depth and contact radius using appropriate physical parameters and equations, as discussed below in section 7.

While the response of the PS surface showed behavior typical of glassy materials such as high stiffness, small  $R$ , and small phase lag, the PEP surface clearly showed different behavior. The small values of stiffness and  $R_{reduced}$  and high phase lag for the PEP surface may be related to the liquid-like character of its surface that results in efficient damping of the tip movement. The behavior of PEP/60 was quite different from that seen for the pure polymer. Since we believe the aged PEP/60 surface is highly enriched in tackifier, its relatively high stiffness is reasonable. However, its very high value of  $R$  as compared to the other surfaces is intriguing. This may be explained if we postulate that the lateral movement of the tip is much more sensitive to the “stickiness” of the surface than is the z-modulation. In our earlier X-modulation study,<sup>32</sup> we argued that the amplitude of the response to the oscillatory forcing function and the behavior of the “stick-slip” transition is very sensitive to the adhesive force between the tip and the sample. This adhesive force should be even more important in the experiment that combines X-modulation with the force-distance curve because the final normal load increases up to 20 nN, resulting in an enhanced interaction between the tip and sample. Again, one finds that the surface of PEP/60 is “sticky”.

**Conclusion:** The combination of X-modulation with a force-distance measurement yields a more precise and reproducible characterization of the surface, while simultaneously providing information on lateral force and sample stiffness.

## 7.) Studying Humidity Effects Effects with X-modulation Combined with Force-distance Measurement

The relative humidity of the environment is known to have a strong influence on adhesion<sup>47</sup> and for the most rigorous exploration of adhesive surfaces using the new technique, humidity must be controlled as an additional experimental parameter. Small variations in behavior with humidity were seen for the PEP surface as shown in Figure 20, where a normalized value of rms response is plotted as a function of time at three forcing amplitudes.  $R_{normalized}$  is given by

$$R_{normalized} = R_{exp} / (F_{max,exp}/F_{max,ref}).$$

$F_{\text{max,ref}}$  is the maximum force from the loading curve in the force-distance measurement for the PEP surface with a forcing amplitude of 0.004 V and 23% relative humidity. At relatively high forcing amplitude, the lateral force decreases with humidity. This is reasonable because even if no strong interaction with water is expected, due to the hydrophobic character of the PEP surface, water can act as a lubricant during tip movement, which results in a reduced frictional force. This trend is consistent with the result obtained from an X-modulation experiment without the simultaneous force-distance measurement.

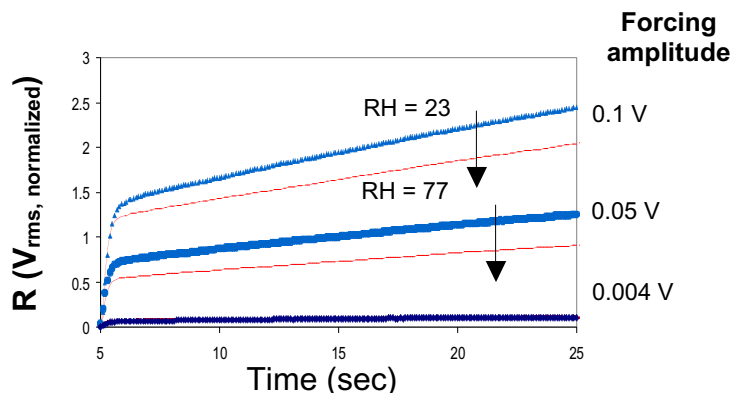


Figure 20. Variation in the X-modulation response with a change in relative humidity from 23 to 77% for the surface of the aged PEP sample when measured using X-modulation in combination with the force-distance measurement. Results are shown for three forcing amplitudes: 0.004, 0.05, and 0.1 V.

The data show that the stiffness of PEP decreases slightly with forcing amplitude at both high and low humidity, even if the order of magnitude is still much smaller than that of PS and PEP/60. It is believed that the normal force is not completely uncoupled from the lateral force, which can result in an extra force being exerted in the direction normal to the surface. This additional force may be increased with increasing sample displacement in the x-direction because  $R$  increases gradually with forcing amplitude, indicating that the tip is

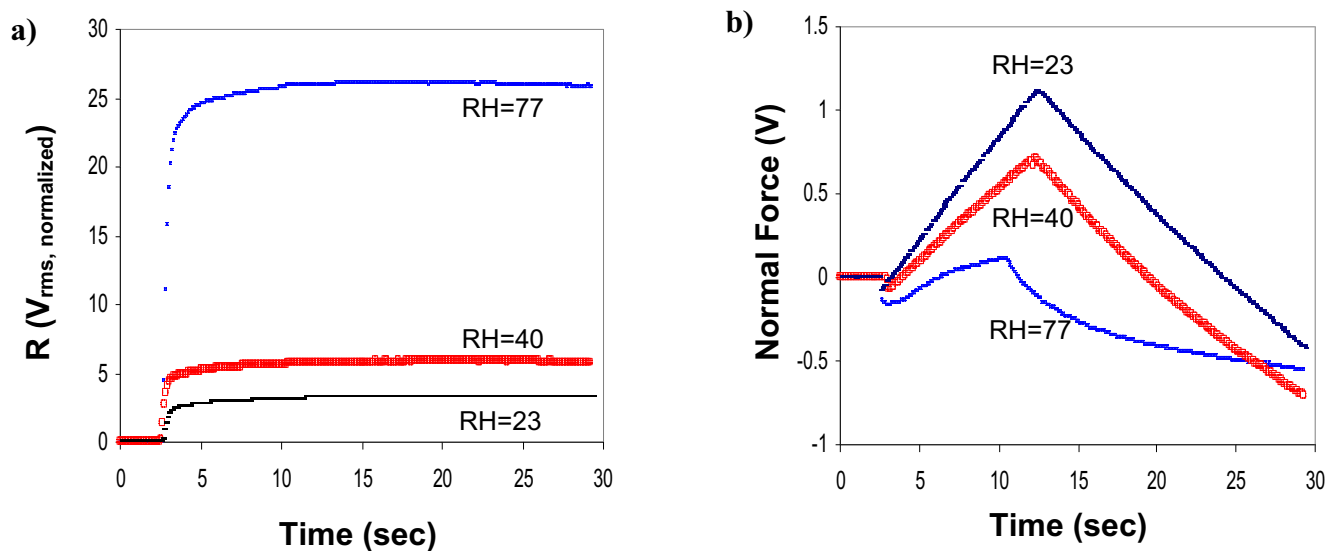


Figure 21. (a) Variation with time in the normalized rms lateral force for the PEP/60 surface at three relative humidities: 23, 40, and 77%. (b) Variation in uncalibrated normal force with time (derived from the A-B signal) for the same experiments for which data are shown in part (a).

stuck to the surface under these experimental conditions. At the same time, however,  $\theta$  decreases gradually with forcing amplitude. Because all measurements were done in the stick regime, this phase change must originate from the viscoelastic nature of the surface and reflect a change in response with shear rate.

The lateral force in response to X-modulation on the PEP/60 surface varied more strongly with humidity than did the response of PEP. Figure 21 shows for the PEP/60 surface the variation of  $R_{\text{normalized}}$  and normal force as a function of time for three different relative humidities. The value of  $R_{\text{normalized}}$  rises rapidly upon initial loading and then remains roughly constant through the remainder of the trace. The rms lateral force increases substantially with humidity. We conjecture that this is due to interaction between the water in the atmosphere and the tackifier. Figure 21b shows traces with time of the normal force, derived from the A-B signal. The trace changes a small amount with the humidity increase from 23 to 40%. The maximum normal force attained decreases and the sample compliance is lower at the higher humidity, as evidenced by the lower slope. Also a small curvature appears in the unloading curve. However, upon increasing the humidity to 77% the maximum force attained decreases dramatically, the time required to reach the end of the loading sequence drops, and a stronger curvature appears in the unloading curve. This behavior is observed because the more hydrophilic nature of the PEP/60 surface results in strong, but complicated, interaction with water. Values of quantitative descriptors characterizing the changes with humidity are summarized in Table 2. At the highest humidity (RH = 77%), the overall stiffness has dropped to around 0.06 N/m, a value similar to that of the pure PEP surface. At the same time the phase lag has increased slightly, but the value of  $R_{\text{normalized}}$  has increased dramatically. We believe this behavior is consistent with the presence of a tackifier-enriched surface. It is highly likely that as a result of the altered interaction at the surface, the tip penetrates more deeply into the sample in the case of the highest humidity. In that case the tip may penetrate to the “bulk” of the sample, which will have a lower hardness than does the surface if the surface is enriched in tackifier (especially after aging). It is also possible that the entanglement density of the polymeric blend near the surface maybe reduced during this nano-scale contact by water molecules transported to the location by the tip.<sup>37</sup> Water can act like a plasticizer. Either effect would result in a smaller normal force being observed. Therefore, we conclude that the PSA surface is enriched in tackifier.

This proposed explanation can be further probed by attempting a more rigorous analysis to obtain values of the penetration depth and contact area. In the previous section, we mentioned briefly the limitations and difficulties in obtaining quantitative results from AFM nanoindentation data. Having acknowledged those limitations, we analyze the force-distance data on the basis of Hertzian contact mechanics. The loading force can be written as<sup>48</sup>

$$F = k_{\text{contact}} \delta \quad (1)$$

because Hooke’s law connects the deflection of the cantilever and the applied load through the force constant,  $k_{\text{normal}}$ , of the cantilever, which is related to the total system stiffness,  $k_{\text{total}}$ , and the contact stiffness,  $k_{\text{contact}}$ . Here,  $\delta$  is the penetration depth of the tip. VanLandingham<sup>44</sup> recently discussed the analysis of the nanoindentation of polymers using a method of analyzing indentation load-penetration curves based on work by Oliver and Pharr<sup>49</sup>. Assuming this approach is applicable to nanoindentation data obtained using SPM, one can calculate the contact depth,  $h_c$ , as shown in Figure 22, by

$$h_c = \delta - \frac{\varepsilon \cdot F_{\text{max}}}{k_{\text{contact}}} \quad (2)$$

where  $\varepsilon$  is a function of the particular tip geometry. Using simple geometrical considerations, the contact radius can be roughly estimated by

$$a = h_c \tan \alpha \quad (3)$$

Since we used a conical tip with a half contact angle,  $\alpha$ , of 32.5 degrees,  $a$  has the value  $2(\pi-2)/\pi$ . Therefore, the elastic modulus,  $E$ , can be calculated using the following equation<sup>7,44</sup>

$$E = k_{\text{contact}} / 2a \quad (4)$$

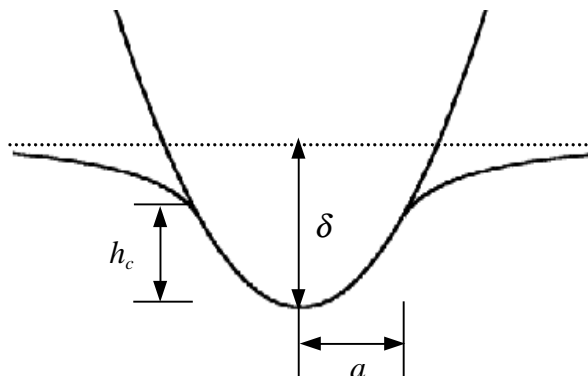


Figure 22. Illustration of the contact geometry.

The Hertz model<sup>45</sup> also gives a relation between penetration depth and the loading force<sup>48</sup>

$$F = \frac{2}{\pi} \left( \frac{E}{1 - \nu^2} \right) \delta^2 \tan \alpha \quad (5)$$

Since we used rubber materials, we assumed a value of the Poisson ratio of 0.5. The results of the analysis are summarized in Table 3. Although there are differences in the values of moduli calculated using equations (4) and (5), the orders of magnitude are the same, which suggests our approach is appropriate.

**Table 3. Values of Modulus Estimated using Herzian Contact Mechanics.**

	RH (%)	$\delta$ (nm)	a (nm)	$E_1^a$ (MPa)	$E_2^b$ (MPa)
PEP	23	143	25	1.8	1.2
PEP/60	23	49	9	26	20
	40	62	11	10	7.8
	77	87	15	2.3	1.8

<sup>a</sup> Calculated using eqn 4.

<sup>b</sup> Calculated using eqn 5.

At normal humidity, the modulus of PEP is calculated to be 1~2 MPa, which seems a reasonable value, though we do not have a measured bulk value to which to compare because this sample has been aged. As mentioned before, analysis of the nanoindentation data obtained by AFM using contact mechanics theory is a nontrivial process. In addition to the critical argument about the validity of applying the contact mechanics to AFM data, there are many uncertainties in the parameter values used. The exact value of the force constant of the cantilever is one important quantity. However, the difference in modulus calculated for PEP and PEP/60 is large enough that we believe relative comparisons are valid, nonetheless. For example, even if we assign an uncertainty of 30% to the value for the normal spring constant of the cantilever, the propagated uncertainty in elastic modulus is only 10~15 %, which does not overshadow the order of magnitude difference in calculated modulus between samples.

At high humidity, while the elastic modulus dropped dramatically, R increased by about 10 times. This is quite an interesting finding. Contact radius and penetration depth also increased over 60 % and this effect by itself might increase the lateral force during sample oscillation. However, the changes in contact radius and

penetration depth are not large enough to explain such a big change in  $R$ . We believe that the sides of the tip may still be in contact with the tackifier rich surface region and the condensed water layer on the surface of the sample, and this may be responsible for the higher lateral force during lateral oscillation of the sample. This idea comes from a comparison with the "rolling ball" method for measuring adhesion. In analyzing results from a "rolling ball" measurement,<sup>47</sup> the frictional force is understood to be the sum of two components, the adhesion component,  $F_{adh}$ , and the deformation component,  $F_{def}$ . The latter is a function of the material properties such as modulus and internal cohesion. However, in the case of PSAs,  $F_{adh}$  must be much larger than  $F_{def}$ . If the quantity  $R$  likewise results from two components, one due to adhesion and one due to deformation, we imagine that such a large enhancement in lateral force is most likely related to an increase in the adhesion component.

The precise way in which the behavior of this nano-scale contact can be related quantitatively to the overall performance of the adhesive must still be explained. We conjecture that the humidity sensitivity seen on the nanoscale may indicate that peel and modulus decrease with increasing humidity because wetting of the adherend by the adhesive is hampered by the presence of a thin layer of water on the surface. Moreover, undesired chemical reaction either within the adhesive or between the adhesive and adherend is possible and water could act as a plasticizer. In any case we take the very different sensitivity to humidity of the PEP and PEP/60 surfaces to be evidence for the presence of tackifier enrichment and we conclude that mediation of the tip-surface interaction by water molecules is very important in nano-scale contacts where the role of tackifier is significant.

**Conclusions:** Using contact mechanics with appropriate simplifying assumptions, results from X-modulation combined with force-distance measurement can be used to estimate the modulus of the surface and changes in it with changes in humidity. A large oscillating lateral force (from X-modulation) and small stiffness (from the force-distance measurement) for PEP/60 at high humidity are consistent both with a model that envisions a tackifier-enriched region within 50~100 nm of the surface and with the hypothesis that at a hydrophilic surface water molecules may strongly alter the surface-tip interactions or modify the mechanical properties of the material nearest the surface.

## Overall Summary

Substantial progress was made during the course of the grant both in understanding surfaces of model adhesive blends and in developing scanning probe methods for studying these surfaces. Work with a new tackifier revealed that for complex commercial tackifiers the mixture of species in the tackifier may benefit miscibility, so that the mixture contains species that alone are not miscible in the adhesive. When miscibility is impaired aging phenomena become more prominent. Using such an adhesive blend it was demonstrated that force-distance curve measurements with the scanning probe can reveal viscoelasticity effects related to frequency dependence, but hysteresis in the piezo and the need for large travel with "sticky" samples limits the frequency range that can be studied.

X-modulation is an excellent technique for probing differences in mechanical properties of adhesive surfaces. However, a characterization protocol combining X-modulation with a force-distance measurement is superior, yielding better reproducibility, higher precision, and more information in one experiment. Humidity effects were investigated using the new protocol and were found to be most pronounced with the aged PEP/60 model adhesive, which we had already shown earlier has the most strongly adhesive surface of the blends of various tackifier composition. The changes in mechanical behavior with humidity for that sample are consistent with plasticization of a tackifier-enriched surface by water or enhanced capillary bridging to the tip due to changes in the surface hydrophilicity caused by tackifier surface enrichment.

## Acknowledgements

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#### TECHNOLOGY TRANSFER

a.) Patent Applications and/or awards

There were no patent applications.

b.) Names and organization of individuals in government, academics, or industry to whom at least one annual report was sent and/or this year's report will be sent:

Dr. Ken Chuang, Research Associate, Avery Dennison Research Center  
Dr. James Barratucci, Truseal  
Dr. Heidi Schroeder-Gibson, Natick  
Dr. Matt Muir, Goodyear Tire and Rubber Company  
Dr. John Willey, Goodyear Tire and Rubber Company  
Dr. Hong Wu, Tesa Tape, Inc.  
Dr. Gary Hagenauer, ARL  
Dr. Stephen McKnight, ARL  
Dr. Nora Beck Tan  
Dr. Georg Böhm, Manager, Bridgestone/Firestone Research  
Dr. Adriana Paiva, 3M Company  
Dr. Xiaoqing Li, Ashland Chemical - Central Adhesives  
Prof. J. Koberstein, U. Connecticut  
Prof. Gary Hamed, U. Akron  
Dr. Doug Kiserow, ARO  
Penny Gray, Goodyear Tire and Rubber Company  
Dr. Mike Mallamaci, Goodyear Tire and Rubber Company  
Dr. Volcker Schmidt, Tesa AG, Adhesives and coatings  
Dr. Ken Shull, Northwestern University

c.) Individuals with whom the work was discussed.

Dr. Seunghun Hong, Research Professor, Northwestern University  
Dr. James Schlademann, Goodyear Tire and Rubber Company  
Dr. Volcker Schmidt, Beiersdorf AG, Adhesives and Coatings dept.  
Dr. Hubertus von Voithenberg, Vice President, Research and Development tesa  
Dr. Yuan Yuan Zhang, Avery Dennison  
Dr. Alamgir Karim, NIST  
Prof. Atsushi Takahara, Institute for Fundamental Research of Organic Chemistry,  
Kyushu University, Fukuoka, Japan  
Prof. Ophelia Tsui, Hong Kong University of Science and Technology, Physics Dept.  
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Prof. Ken Shull, Northwestern University  
Dr. Al Crosby, NIST,  
Dr. Hong Wu, tesa tape, inc.  
Dr. Stephen McKnight, ARL  
Dr. Michael Kent, Sandia National Laboratory  
Dr. Jack Houston, Sandia National Laboratory  
Prof. Jürgen Rühe, University of Freiburg, Germany  
Prof. Vladimir Tsukruk, Iowa State University  
Dr. Kathryn Wahl, NRL  
Prof. William Unertl, U. Maine

d.) Breakthroughs

- Frequency dependence of force-distance curves of adhesive surfaces measured for the first time.
- Evidence of segregation of low molecular weight species to a surface of a blend observed without the aid of a chemical distinction between the blend components for the first time.
- X-modulation technique applied for the first time to an adhesive material.
- Enhanced X-modulation technique with force-distance curve applied to adhesive material for the first time.
- Changes in surface modulus of tackified adhesive with humidity estimated quantitatively for the first time.